FROM HOME TO COMMUNITY TO CITY: DIFFERENT APPROACHES TO ENVIRONMENTAL EXPOSURE ASSESSMENT OF PARTICULATE MATTER ACROSS THE PITTSBURGH REGION

by

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ABSTRACT

Air pollution is a global public health issue, and regulations such as the Clean Air Act of 1970 in the United States were created to control emissions and clean up the air that we breathe. The city of Pittsburgh, Pennsylvania, has a rich history with regards to air pollution and is a unique study area, with varying topography of hills and river valleys, active industrial plants such as steel mills and coke works, and high traffic density areas. Fine particulate matter ($PM_{2.5}$) and black carbon (BC) are known to be associated with respiratory and cardiovascular disease, and meteorological effects such as the presence of inversions can result in trapping of $PM_{2.5}$ and BC. Air pollution studies were performed at differing exposure levels, from within the homes of asthmatic children, to a community with an active steel mill, and to a specified domain of across the city of Pittsburgh. This hierarchy of sampling occurred via a variety of exposure assessment methods, from personal exposure monitors, mobile monitoring devices, and stationary sampling units.

Spatial and temporal variability of pollutants is seen at all levels of sampling, and $PM_{2.5}$ and BC were modeled via multivariate and land use regression (LUR). Pollutant concentrations in Braddock and Clairton were higher indoors compared to outdoors, with smoking accounting for much pollutant variability. Mobile monitoring, which can be a preliminary step in any field study design, found higher $PM_{2.5}$ and PM_{10} concentrations in Braddock during morning hours

compared to the afternoon, along with a strong presence of inversions. For citywide sampling, exposure surface maps were derived from LUR models and could be used for epidemiological health effects studies. A combination of these exposure assessment methods used around Pittsburgh could be replicated in other areas to fully understand public health exposure and source apportionment within a home and across a specific area of interest.

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PREFACE

I would like to acknowledge my mentor, Dr. Jane Clougherty, for providing the opportunity to study exposure assessment across Pittsburgh, as well as providing travel to various conferences, such as the International Society for Environmental Epidemiology (ISEE) and International Society of Exposure Science (ISES) from Seattle, Washington to Barcelona, Spain. I would also like to acknowledge Jane for working on a potential study in New Zealand this upcoming March and April 2014. She has provided me with opportunities, international experience, and memories that I will remember the rest of my life.

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1.0 INTRODUCTION/BACKGROUND

The focus of my work at the University of Pittsburgh's Graduate School of Public Health has been centered on air pollution, especially fine particulate matter ($PM_{2.5}$) and black carbon (BC). Air pollution is a global environmental public health issue that affects millions of people on a daily basis, from personal exposures within the home, to across the community, as well as countywide. The purpose of this dissertation is to provide background on air pollution and discuss the various environmental exposure assessment methods and hierarchical levels of sampling that can be used to determine pollutant concentrations. The hypotheses for this dissertation are 1) Pittsburgh's air quality is improving, but intra-urban variability exists, 2) source apportionment methods leveraging the elemental composition of particulate matter can help disentangle urban source contributions, and 3) outdoor concentrations and indoor sources contribute to indoor air quality in industrial communities. By studying Pittsburgh, Pennsylvania, one can see the transformation from a highly polluted city based on steel production to a service economy. However, air pollution remains a problem in specific communities within the Pittsburgh area and other cities. This dissertation focuses on a public health approach geared toward protecting communities using the results from exposure assessment and subsequent development of models and exposure surface maps. Exposure surface maps for $PM_{2.5}$ and BC in Pittsburgh can be used in epidemiological studies. Useful background and data analyses of

Pittsburgh are provided for community and public health professionals, as well as local policy decision makers.

Historically, pollution has been identified as a sign of industrialization, but studies soon began to link air quality with health issues [1-9]. Concern about air pollution in the United States was dramatized by extreme pollution episodes, including the 1948 stagnation/smog incident in Donora, Pennsylvania, resulting in 7,000 illnesses and 20 deaths [10]. The Donora episode showed the relationship between acute health effects and high levels of air pollutants. For industrialized countries like the United States, respiratory illness and death rates are significantly higher in areas where higher pollutant concentrations have been found [11].

By discussing the history of air pollution and focusing on various exposure assessment studies in Pittsburgh including within the home, a community, and county, one can demonstrate the great strides that have been made to yield a cleaner ambient environment, as well as provide a framework for other cities to use similar sampling approaches. Air pollution travels across countries and geographic boundaries, making it a serious public health issue. Developing and improving global multi-pollutant indicators of health and economic effects of air pollution are necessary to assess air quality improvement around the world [12]. A home to community to city hierarchy for analysis can demonstrate pollutant variability and determine significant sources of pollution. Through a literature review, as well as various field work campaigns in Pittsburgh, objectives of this dissertation are to educate the community on air pollution and its severity, as well as providing a template of several exposure assessment methods that could be duplicated in cities other than Pittsburgh. Additionally, a better understanding of intra-urban variability in an area with unique terrain and frequent atmospheric inversion events could be pursued using these exposure assessments. Furthermore, pollutant exposure surface maps for

Pittsburgh were created and could be used for epidemiological health cohort studies. Two particular areas that have operating steel plants and coke works are in Braddock and Clairton, Pennsylvania, located directly where specific wind patterns, combined with the presence of inversions and river-related meteorological effects can blow pollution into more populated areas (i.e. downtown Pittsburgh). Even though areas in Pittsburgh have concentrations of contaminants that fall below national standards, some fail to do so, and this can therefore affect all who live or travel in the vicinity.

Air pollution began as a global problem, needing several regulations so that a cleaner environment could be achieved. Contaminants not only affect the air, but also the water, which can therefore harm ecosystems and wildlife [13]. By providing fieldwork within homes of asthmatic children and across a set of sites in a town encompassing an active steel mill, one can make a judgment as to whether the air pollution problems have to be addressed in local areas like Braddock. Sampling campaigns across 37 distributed sites in Allegheny County can show intra-urban spatial and temporal variability patterns of fine particulate matter and black carbon; different modeling approaches can be used to predict this variability in air pollution concentrations and will be discussed further. Furthermore, source apportionment using trace metals data from the $PM_{2.5}$ that was collected could provide specific details on pollution's contributors. It may be more beneficial to regulate constituents of a pollutant during peak hours of exposure, such as a timeframe where frequent inversion events are trapping pollution near ground level.

1.1 HISTORICAL PERSPECTIVE ON AIR POLLUTION

1.1.1 What is Air Pollution?

Air pollution can be defined as any constituent present in the atmosphere as a result of anthropogenic (man-made) activity or natural processes that causes harmful effects to humans, animals, and the rest of the environment, and was until the late 1960's, a problem of growing importance [13]. However, over the past 40 years, new regulations, regulating agencies, and national standards have been developed to address major air pollution problems [14]. Still, in cities such as Beijing, China, during the winter season, air pollution is a growing problem. Though reducing pollution levels is the ultimate goal, there is no possibility of removing all the pollution from the air since combustion processes are a necessity and not all pollution is of anthropogenic origin. The problem is ensuring that air polluters disperse residuals to the point where damage suffered by a society is minimized or eliminated [2].

Sources of emissions can be broken down into different categories: 1) Point sources include factories, power plants, and large scale emitters, 2) area sources include home heating sources and smaller sources that are nearly impossible to monitor over time, and 3) mobile sources, such as motor vehicles, airplanes, trains, and other line sources. There has been substantial improvement in developed countries in controlling emissions from all three types of sources, with the use of better filters, catalytic converters, changes in fuel, and fuel injected engines. Globally, the largest source of air pollution is combustion, and it is estimated that 15% of hydrocarbon emissions result from burning of oil, natural gas, coal, and wood.

Particulate matter, a complex mixture of small and large particles and liquid droplets, is of important concern in the Pittsburgh area. Its composition is not homogenous since it can be

made up of many components, such as acids (nitrates, sulfates), organic chemicals, metals, and soil/dust particles [15]. For studies that will be discussed later, overall $PM_{2.5}$, black carbon, and a suite of trace metal constituents will be of interest. With regards to particulate matter, the size can be a direct link to potential to cause damage to the human body. The Environmental Protection Agency (EPA) is concerned about particles that are 10 micrometers in diameter or smaller because they could travel through the nose and throat towards the lungs. When these particles are not cleared and make it in the lungs, these fine particles can lead to heart and lung issues. Two primary categories of particles are inhalable coarse particles and fine particles. "Inhalable coarse particles" can be found near roadways and dusty industries, are larger than 2.5 micrometers and smaller than 10 micrometers in diameter. "Fine particles" are part of smoke, smog, and haze, and they are less than 2.5 micrometers in diameter. They can be directly emitted from forest fires, or they can form when gases emitted from power plants, industries and automobiles react in the air [15]. A recent study has shown consistent seasonal concentrations of $PM_{2.5}$ in the Pittsburgh region, and sulfate was the primary component of particulate matter [16].

1.1.2 Health Effects from Air Pollution

Air pollutants have been known to cause respiratory and cardiovascular problems [9, 17, 18]. Studies of the respiratory system have shown that air pollution has contributed to bronchitis, pulmonary emphysema, lung cancer, pneumoconiosis, cough, and chest pain. Health effects from air toxics include cancer and respiratory irritation, as well as reproductive, pulmonary, and liver toxicities. Long-term exposure to outdoor air pollutants seems to increase the prevalence and incidence of bronchitis, cough, and decreased lung function [17]. It has been found that reductions in $PM_{2.5}$ concentrations were associated with a reduced mortality risk;

cardiovascular disease and lung cancer have been linked with ambient $PM_{2.5}$ concentrations [3]. Many studies have reported significant associations between $PM_{2.5}$ and all-cause mortality[18].

Studies have documented increased respiratory illness in children in association with PM exposures, and decreased peak flow has been observed [19]. Diesel exhaust particulate has been found to induce airway inflammation in normal subjects, and asthma admissions have been found to increase by 2.7% over mean levels for each 12 $\mu g/m^3$ increase in PM_{10} [19, 20]. Interestingly, a relationship between diabetes and $PM_{2.5}$ concentrations has been studied, suggesting that there is a 1% increase in diabetes prevalence with a 10 $\mu g/m^3$ increase in $PM_{2.5}$ exposure [1]. In China, respiratory and cardiovascular sickness and death rates are significantly higher in polluted as opposed to non-polluted areas. One estimate claims that nearly 50 percent of respiratory ailments are related to excessive air pollution, so the public health relevance cannot be underestimated; smoking is another key component and will be addressed in indoor air sampling [11]. A study by Somers et al exposed laboratory mice to areas where steel mills resided, and heritable mutation frequency was 1.5 to 2.0-fold elevated compared with mice at a reference site; therefore, populations living near steel mills may be at a risk of developing germ line mutations more frequently based on chemical concentration [5]. A unique example of air pollution and adverse health effects is the Utah Valley Steel Mill, which opened in 1986, closed in 1987, and re-opened in 1988, providing a major source for particulate matter. The changes in mortality and morbidity data at hospitals in the area correlated with the mill being open or closed, as numbers were higher in 1986 and 1988 and lower in 1987 when the mill was closed [21]. Studying an area close to a steel mill in Pittsburgh will be discussed later in this review. Not only does pollution affect humans: plant life is sensitive to ozone (O_3), so forest ecosystems and agricultural crop production are also a concern [13].

Another important issue is that air pollution does impose major economic costs, due to a combination of premature mortality, increased sickness and lost productivity, as well as a decrease in crop yields and ecosystem impacts. A cost-benefit analysis based on the Clean Air Act in the United States has shown that reduction in emissions has provided greater benefits at a ratio of up to 40 to 1 [11]. A recent study has concluded that a decrease in 10 $\mu g/m^3$ in the concentration of fine particulate matter is associated with an increase in life expectancy of 0.61 (± 0.20) year [22]. It may be difficult for the public to see the severity because pollution does not typically lead to immediate mortality; it can be a chronic source of exposure that causes damage after contact for several years in a particular area, but exposure depends upon how high pollutant levels rise. Past episodes in Donora and London show affects from dangerously high pollutant levels. Today, pollutant concentrations are reaching dangerously high levels in Beijing, China, especially in the past few winters, where a combination of weather haze, heating from coal-fired power plants, increasing car ownership, and increasing industrial activity are causing smog levels where fine particulate matter concentrations are greater than 600 $\mu g/m^3$ [23, 24].

1.1.3 Air Pollution's Storied Past: Attempts to Control

Air pollution has a long, storied history when dealing with health issues that have arrived from emissions. Roman philosopher Seneca wrote about the heavy air of Rome in 61AD. Regulations regarding air pollution were introduced by Edward I in 14th Century England based on the burning of sea coal, and violators were tortured for producing foul odors [11]. The first air pollution regulations in the United States dealt with coal, resulting in ordinances being passed in the 19th Century for Chicago, St. Louis, and Cincinnati focused on regulation of smoke and SO_2 emissions. Extreme air pollution episodes like the 1948 incident in Donora, Pennsylvania

and the 1952 London Fog dramatized effects of particulate matter on human health. Events where severe cases of injury and death occur can put an issue such as air pollution into perspective. The British Clean Air Act was passed in 1956, focusing largely on smog and reducing dark smoke, and it was further revised in 1968 to enforce taller smoke stacks on buildings. London introduced smoke control in 1661 [25].

In the 1940s, Pittsburgh had a public protest against smoke, leading to slight changes in fuels and combustion practices, as well as promises that air would be cleaned by using treated local coal [26]. Also at the same time, California began to study the causes and effects of photochemical smog. The London Smog episode of 1952 impacted thoughts on air pollution within the United States. In 1952 after the London incident, Oregon became the first state to have an air pollution control agency [11]. State and local air pollution agencies made efforts to control air pollution in the 1960s, and levels of SO2 and soot decreased significantly. Between 1900 and 1970, emissions of nitrogen oxides increased 690 percent, volatile organic compounds increased 260 percent, and sulfur dioxide increased 210 percent [27]. The United States EPA was established in the 1970s, and emissions of these pollutants have continued to decrease since the 1970 Clean Air Act was passed. In major cities, decreases were seen even before the 1970 Clean Air Act was passed, particularly in the mid to late 1960s. However, only recently did the country begin to see major decreases in ozone levels.

Following the passage of the 1970 Clean Air Act, requiring National Ambient Air Quality Standards (NAAQS), emission levels for hazardous air pollutants, and control on mobile source emissions, the United States continued improvements in air quality, while maintaining a growing but changing economy that would benefit the public and their health [11]. The Clean Air Act of 1970 provided a strategy by which to monitor and evaluate air quality by enforcement

of NAAQS, which consists of primary and secondary standards. Primary standards are enforced to protect public health, especially for sensitive people like children, asthmatics, and the elderly. Secondary standards set limits to protect public welfare by managing reduced visibility, monitoring damage to animals, crops, and vegetation, and regulating buildings [27]. The EPA set national air quality standards for the following six criteria pollutants: carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO_2), ozone (O_3), particulate matter ($PM_{2.5}$ and PM_{10}), and sulfur dioxide (SO_2). It is important to note that ozone is not directly emitted to the air; it is formed when the sunlight acts on emissions of nitrogen oxide (NOx) and volatile organic compounds (VOCs). Ozone is called a secondary pollutant, while the rest are called primary pollutants. Even though improvement has been observed, there still are areas that are violating the regulations.

The United States was not the only country to take note of the severity of the air pollution issues. The Law of the People's Republic of China on the Prevention and Control of Atmospheric Pollution was passed in 1987 with amendments in 1995 and 2000 [11]. In China, a very short period of fast economic growth has led to higher living standards; however, it has also caused severe problems in environmental pollution, making it a significant public health issue [28]. Because populations like China continue to grow, there will be a greater demand for more energy use, and the cleanest and most environmental-friendly methods for business and recreation need to be employed. Pollutant concentrations have been very high in Beijing this past winter 2013, indicating that further enforcement and regulation is needed before another episode such as that in Donora or London occurs. It has been suggested that short-term risks do pose significant health effects at air pollution levels at the minimum standard in China [29]. Unfortunately, few studies have examined long-term effects in China as compared to North

America and Europe [28]. The United States and China are noted for being the top two energy consumers worldwide; therefore, they are also the top two emitters of numerous air pollutants that can impact the globe [11]. Improving air quality has become an urgent task in the United States and China, as well as other countries.

1.1.4 Donora, PA Stagnation and the London Fog

In October of 1948, a severe stagnation episode occurred in the Pittsburgh area, lasting 4 days [30]. While the impact was more widespread, it had a particular effect on Donora, a mill town on the Monongahela River, 15 miles from Pittsburgh (Figure 1). In some steel, zinc is one of the metals used to coat steel in order to prevent rust; Donora was home to about 14,000 inhabitants and the Donora Zinc Works. During the stagnation episode, air pollution increased, and the impact on health started to become noticeable as individuals experienced severe respiratory problems with some deaths [3]. Doctors recommended evacuation of those with respiratory problems, though this was hampered by traffic congestion and the severe smog. By the end of the episode, 20 deaths occurred and 7,000 additional individuals were ill. Pittsburgh was not as severely affected as Donora, primarily because the wind was not blowing towards the city. In 1945, prior to the Donora episode, the mayor of Pittsburgh, along with the city elite, had begun to identify actions to improve air quality, such as reducing the use of bituminous coal as part of a 1941 smoke ordinance [31]. Natural gas was piped into homes for heating, and diesel engines began replacing coal-fired engines in locomotives and riverboats.

Figure 1. Photograph from the Pittsburgh Post-Gazette of Donora, PA at noontime during the deadly smog event of 1948 [24].

The significant incident that made individuals all over the world aware of air pollution was the London Fog of 1952. It is important to note that London has had air pollution problems prior to this stagnation episode. Because England experienced colder-than-average temperatures, they burned great amounts of coal to heat their homes. Winds carrying particulate matter and gases from distant factories joined the industrial pollution in London [25]. A number of weather conditions resulted in radiation fog and smog that would not lift for a few days, resulting in stagnation; during the smog, pollution was released into the atmosphere. Measurements at London's County Hall showed that the concentration of smoke increased from 490 $\mu g/m^3$ on December 4th to 4,460 $\mu g/m^3$ on December 7th and 8th. Concentrations were as high as 7,000 $\mu g/m^3$, and as a result, this caused nearly 4,000 deaths and was implicated in another 8,000 deaths in the following months.

1.1.5 A Perspective on Pittsburgh's Air Pollution Story

Globally and locally, air pollution has been a problem, with Pittsburgh being one of the longest documented histories of pollution and efforts to clean the city up. Pittsburgh established itself as the "smokiest" city in the country mainly due to its abundant supply of coal in the 18th and 19th Century [26]. In the early 19th Century, industry began to boom, and steel production became a significant driving force. Producing steel requires much energy, which is provided by coal, and coke that is used in the smelting process is made from coal. Steel mills and coke ovens began to develop along the three rivers, particularly the Monongahela River, and steel was transported via the rivers and railroads. As the amount of steel production increased, so did the air pollution. During a morning in Pittsburgh at 9:20am, the city still looked like night, and street lights were kept on continuously.

Following protests in the 1940s, the Pennsylvania Railroad shifted from coal-burning to diesel-electric locomotives in an attempt to improve air quality in the 1950s. The piping of clean natural gas from the southwest reduced smoke in the area, and soot could then be cleaned off of buildings; unfortunately, the iron and steel industry refused to provide greater control of their effluents. In the 1970s and 1980s, Group Against Smoke and Pollution (GASP) encouraged local enforcement of the Clean Air Act, which brought about slight improvement. The most substantial air quality improvements occurred because of the collapse of the iron and steel industry in the 1980s [26].

When people consider moving to Pittsburgh, Pennsylvania, air quality may be a factor that comes to mind. Many reports come out with Pittsburgh routinely ranked near or at the top of the list for the country's worst air [32]. These reports are misleading due to a monitor in the Liberty Borough area, which is mainly influenced by the Clairton Coke Works and perhaps

ETSW. The appearance of this city has drastically changed, as lights are no longer kept on all day, soot is not found on cars, and people do not have to take an extra shirt to work. Pittsburgh has made substantial strides in cleaning up its air over the years. An assessment of Pittsburgh-related air pollution and health studies has shown that exposure to Pittsburgh air pollution levels has resulted in increased risk of adverse health effects, such as premature death, exacerbation of lung and heart disease, and adverse birth outcomes [33]. This indicates that current exposure assessment of air pollution across Pittsburgh is essential in developing exposure surface maps that can be linked to health effects, as well as source apportionment studies to determine where pollution is coming from. Exposure assessment of particulate matter and black carbon was conducted from personal exposures within the home, mobile monitoring in the Braddock community, which encompasses an active steel mill, and saturation monitoring of air samplers across 37 citywide sites throughout Pittsburgh and the surrounding county.

1.2 APPROACHES TO ENVIRONMENTAL EXPOSURE ASSESSMENT

For the sampling campaigns that will be discussed later in this dissertation, there are a variety of environmental exposure assessment methods to quickly collect pollutant concentrations of concern. For these studies, the primary pollutant that was investigated was fine particulate matter, along with constituents such as black carbon and trace metals. Sampling methodology of particulate matter varied at hierarchical levels from personal exposures within the home to monitoring sites across Allegheny County.

Indoor air sampling was performed on 21 homes during the summer and winter months, in which many residences had a child with severe asthma. The majority of the homes were

located near an active steel mill (Edgar Thomson Steel Works) or an active coke works (Clairton Coke Works). Pollutants collected included fine particulate matter and nitrogen dioxide, and black carbon and trace metals were analyzed from the $PM_{2.5}$.

Moving outside of the homes, a mobile monitoring campaign was performed during the summer and winter, in which 25 designated stops were sampled throughout the community of Braddock, to collect fine and coarse particulate matter. The units used for mobile monitoring were light-scattering nephelometers designed to capture real-time $PM_{2.5}$ and PM_{10} concentrations.

Mobile monitoring was used to quickly assess real-time particulate matter in Braddock, and stationary monitors were deployed at 37 designated sites across a 150 m^2 domain of Allegheny County over a period of two years (two summer seasons and two winter seasons); the first year focused on morning inversion-based sampling, whereas the second year focused on 24-hour integrated sampling. Custom-designed sampling boxes were mounted to a base plate on telephone poles, collecting $PM_{2.5}$ via a Harvard Impactor. Reflectometry was used on all $PM_{2.5}$ filters, in order to determine the percent reflectance and an black carbon absorbance value. These various sampling methods were used to collect pollutant concentrations from a variety of areas of differing sizes, and spatial and temporal variability could be assessed, as well as pollutant-specific modeling and source apportionment. Further information on sampling technologies and instrumentation will be discussed in the next section.

1.2.1 Instrumentation

For mobile monitoring, Hazdust monitors (Model EPAM-5000), light scattering nephelometers, sampled continuous outdoor $PM_{2.5}$ and PM_{10} measurements. They operated at 4.0

L/min and used an EDC-supplied inlet nozzle with a cut-off of 2.5 µm (aerodynamic diameter) for $PM_{2.5}$ measurements. During each sampling day, a $PM_{2.5}$ and a PM_{10} monitor were placed on the backseat of a passenger vehicle. The monitors sampled and recorded concentrations at 10-second intervals over a designated route (Figure 2).

Figure 2. Nephelometer and mobile monitoring sampling route with elevation scale.

The main use of a nephelometer is for air quality monitoring of particulates across a specified area. This occurs when particulates (nozzles are fitted in the device to measure fine or coarse PM) are measured by employing a light beam and a light detector, which is set to one side of the light beam, often at a 90 degree angle. Based on the characteristics such as density (shape and reflectivity) of the $PM_{2.5}$ or PM_{10}, light is reflected into the detector. A mie nephelometer was used for mobile monitoring, involving the scattering of electromagnetic radiation by a sphere ($PM_{2.5}$ or PM_{10}), and a Mie formula/solution is used for analysis; Mie scattering occurs when particles in the atmosphere are the same size as the wavelengths being scattered [34, 35].

For measurement, the incident plane wave, scattering field, and internal field within the units are expanded into radiating and regular spherical vector wave functions, allowing the calculation of the electric and magnetic fields inside and outside the particulate [35]. This function is used to determine how much light is scattered, resulting in Mie resonances (strong or weak scattering of light based on particulate size) [35, 36]. In addition to a quick way of obtaining real-time measurements, the existence of Mie scattering resonances make nephelometry a useful approach for using scattered light to measure real-time particle size, such as $PM_{2.5}$ and PM_{10} collected across Braddock, PA. In comparison to Mie, other scattering such as "Rayleigh scattering" (for smaller particles) and "Rayleigh–Gans–Debye scattering" (for larger particles) are demonstrated [37].

Whereas mobile monitoring can be used to collect real-time pollutant concentrations, citywide saturation involves deployment of stationary monitoring units and gravimetric analysis. Using a temperature (20°C) and relative humidity (35%) controlled glove box (PlasLabs Model 890 THC), 37mm Teflon filters (Pall Life Sciences) were equilibrated for 48 hours and then pre-weighed using an ultramicrobalance (Mettler Toledo Model XP2U) before deployment at monitoring locations. After collection of the samplers, the filters were then post-weighed under the same conditions in the glove box. The ultramicrobalance operates in micrograms to 1 decimal place, and it is located in a firm, vibration-free location on top of a granite table, which is as level as possible and away from direct sunlight. A HAUG Ionizer is also inside of the glove box for removal of electrostatic charge from the filters. All sample filters are equilibrated (set inside the hood, with Petri dish lids ajar, to condition to temperature and relative humidity) to the EPA federal reference method (temperature 20 - 23 °C and relative humidity 30–40 percent) for 48 hours prior to all weighs. For a typical weighing session, two reference filters and a set of ten

filters were weighed twice. If the two filter weights do not agree within the allowed tolerance of ± 5µg, the filter must be re-weighed.

Sampling units were custom-designed to capture integrated street-level samples of $PM_{2.5}$ (Figure 3) [38]. Sampling instruments, including Harvard Impactors (Air Diagnostics and Engineering Inc.) with 37mm Teflon filters and a HOBO data logger (Onset Computer Corporation), were contained in waterproof Pelican cases. The Harvard Impactor (HI) was designed to collect fine particulate matter ($PM_{2.5}$) at a flow of approximately 4 liters per minute (LPM). Two Impactor plates (with a drop of mineral oil) are fitted inside the HI, and these plates collect particulate that is larger than $PM_{2.5}$. Instruments were programmed for specific hours of sampling using a chrontroller (ChronTrol Corporation). For example, the air sampling units could be programmed to turn on and sample Monday through Friday from 6-11AM each day. A tetraCal volumetric air flow calibrator (BGI Instruments) was used to calibrate the air flow to approximately 4.0 LPM, based on the forecasted temperature for the upcoming sampling week. The HOBO data logger recorded temperature and relative humidity at fifteen minute intervals at each sampling site.

Figure 3. Air pollution samplers at a reference monitoring site, with the HI inlet circled.

Black carbon was measured (in absorbance units) from each Teflon filter using an EEL43M Smokestain Reflectometer (Diffusion Systems). Gray and white calibration tiles, as well as a control filter blank were measured throughout the analysis. The filter was placed into a white filter holder cassette, and then placed onto the white calibration tile. Then the light source was placed over the filter, measuring the absorbance of light based on the constituents collected on the filter. Percent reflectance was determined by the device, as a lower percent reflectance would indicate a higher absorbance reading; this occurs based on the color of the filter, and how much of the light source is absorbed by the black components of the $PM_{2.5}$. The light that is reflected is based off of the white tile behind the filter. The absorption and reflection of visible light on the particles is dependent on the particle concentration, density, refractive index, and size [39]. Elemental carbon (also referred to as "black carbon") is the most highly absorbing

component in the visible light spectrum, as soil, sulfates, and nitrates have significantly lower absorptions [40]. Other components with higher absorptions are not expected to be found in the air, so it is assumed that the light absorption is due to elemental carbon.

Another method called the thermal/optical reflectance method has been adapted by several laboratories for the quantification of organic and elemental carbon on quartz-fiber filter deposits [41]. A thermal/optical reflectance method of carbon analysis is currently ongoing for a separate study across downtown Pittsburgh, as well as the reflectance method discussed above. Further comparisons of the predominant thermal and optical methods are needed to better understand and characterize the differences and uncertainties in elemental carbon values [42]. For this past winter, a correlation of 0.82 between thermal/optical and reflectometry readings has been identified, and further comparisons will be made.

After the $PM_{2.5}$ filters are analyzed by reflectance for BC, they are then analyzed for trace metal constituents using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is an analytical technique used for elemental determinations, such as the trace metal constituents that will be assessed for source apportionment. Unlike reflectometry, the Teflon filter is dissolved using this process. In principal, an ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source (converts atoms of the trace metals in the sample to ions) with a mass spectrometer (separates and detects the ions) [43]. The sample is introduced into ICP plasma, an ionized argon gas consisting of positive ions, at 6,000 °C as aerosol droplets, and the solid sample (i.e. filter-based $PM_{2.5}$) is dissolved into a nebulizer [44, 45]. The ICP torch generates the argon plasma. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated, and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma [44]. These ions are then brought into a mass

filtering device called a mass spectrometer through use of interface cones, which transmit the ions in the argon sample stream (at 1-2 torr atmospheric pressure) to a low pressure area (<1 x 10-5 torr) of the mass spectrometer [44]. The ions from the ICP source are focused by the electrostatic lenses in the system (ions and the electrostatic lens both have positive charges, serving to collimate the ion beam and focus it into the slit of the mass spectrometer). Once the ions enter the mass spectrometer (often a quadruple mass filter), they are separated by their mass-to-charge ratio. Alternating and direct current (AC/DC) are applied to opposite pairs of the rods, and then quickly switched along with a Radio-frequency field, in order to establish an electrostatic filter, only allowing ions of a specific single mass-to-charge ratio to pass through the rods to the detector [44]. Upon exiting the mass spectrometer, ions strike the first dynode of an electron multiplier (the detector), releasing a cascade of electrons, which are amplified until they become a measureable pulse [45]. Typically, for each filter collected in indoor and outdoor studies in Pittsburgh, 51 trace metal constituents were measured and nanograms/filter was reported. These weights were converted to ng/m^3, which will be shown in source apportionment.

Indoor air sampling used custom-designed boxes to collect $PM_{2.5}$. Indoor air sampling included the base of the sampling box and the dish hood that stores samplers. This monitor measures particles in the air using a Harvard Personal Exposure Monitor (PEM) connected to a Medo pump via a tube (Figure 4). The PEM was specifically designed to collect fine particulate matter in a similar manner as the Harvard Impactor used for citywide saturation. Because it is so small, it is clipped onto a stand so it can't be knocked over. The stand is placed on a small box so it is not sitting on the ground. This device runs the entire time of sampling, and it is very quiet, as it was designed for use in hospitals. The Ogawa passive filter badge measures nitrogen dioxide and is known as a "passive" badge because it does not use a pump and has no moving

parts. This small device weighs less than an ounce, and it was clipped onto the stand holding the PEM. There are no safety risks from the badge, but because the exposed surface of the badge is where the pollution is absorbed, it needs to be unobstructed. Like citywide sampling, a HOBO device was used to measure temperature and relative humidity, and it is attached to the stand with the other sampling equipment. This device is launched using a computer, and it can record temperature and relative humidity at intervals of every 5 minutes. For indoor, the same procedures from outdoor sampling are followed, including pre- and post-weighing of Teflon filters in a temperature and relative humidity controlled glove box, reflectance for determining BC, and ICP-MS for determining elemental constituents.

Figure 4. Assembled indoor sampling unit.

1.2.2 Hierarchy: Home to Community to City

Personal exposures to air pollutants, such as particulate matter, occur throughout a variety of locations. Pollutant concentrations may be higher within the home compared to outside levels. Thus, it is important to assess particulate matter inside, since the majority of time can be spent indoors. Sampling from within homes located near active steel mills and coke works is used to provide clarification and influence of outdoor sources of pollution. Indoor air pollutants were collected using custom designed boxes and personal exposure monitors. Trace metals data was obtained from filters used to collect particulate matter, and source apportionment was performed on the data.

An indoor air pollution questionnaire was administered to participants, and it is attached in Appendix A. This questionnaire asked questions about occupancy, activities within the home such as cooking, smoking, and cleaning, as well as presence of pets and mold. From these data, a variety of covariates could be created and correlated to pollutant concentrations for multivariate modeling (e.g. smoking frequency, cooking tendencies, open windows).

Mobile monitoring is a quick way to collect real-time fine and coarse particulate matter across a specific area of interest. We used HazDust devices, which are light-scattering nephelometers, to collect $PM_{2.5}$ and PM_{10} over a designated route with specific stops near and within Braddock, PA. This is where an active steel mill, the Edgar Thomson Steel Works, resides. By repeating the same route approximately 40 times at the same specific timeframe, an idea of exposure intensity across this community could be measured each day.

For an outdoor Pittsburgh saturation sampling campaign, 37 sites across a GIS-derived specific domain of Allegheny County were chosen based on traffic density, elevation, and proximity to industry, and summer and winter sampling was performed over a two year period.

This allowed us to examine spatial and temporal variability and build land use regression models in order to estimate pollutant concentrations at unmonitored sites. This saturation campaign, combined with temporally adjusting $PM_{2.5}$ and BC, allowed us to see spatial and temporal variability over an entire city, with the eventual goal of developing pollutant exposure surface maps from land use regression models. These various sampling methods performed exposure assessment across areas of differing sizes and emission sources.

1.2.3 Using Geographic Information Systems (GIS) for Sampling

Geographic Information Systems (GIS) is used to display and manage geographical information, allowing for spatial data visualization and data manipulation. For our purposes, we are interested in overlaying the Pittsburgh region with a suite of covariates of interest, such as traffic roadways, industrial point sources, and elevation grade with the goal of creating a smooth surface map developed from LUR modeling. Two standardized methods of exposure assessment characterize for the variability of PM within an area of interest, including spatial saturation monitoring followed by land use regression modeling and source apportionment [46-50]. Each was employed in this study. Covariates regarding local pollution sources, such as industrial emissions, land use parcels, and kernel traffic densities are created using GIS. Information such as traffic density, elevation, and proximity to industry could be determined via GIS, and used to systematically allocate monitoring sites. This could allow us to spatially saturate a unique and complex domain, such as the one in Pittsburgh and surrounding Allegheny County. After completing the analyses, LUR could then be performed to model pollution concentration estimates (i.e. particulate matter or black carbon) at locations where monitors were not used.

Monitoring locations could be randomly selected based on pollution source distributions [51]. Data created in GIS can indicate fine-scale spatial variability in local terrain via various mapping techniques, and potential modifiers of pollution concentration, such as elevation, could be included in sampling methodology and LUR modeling [52, 53]. GIS-based indicators of local pollution sources and topography were created to systematically select air monitoring sites across our domain of Allegheny County. Monitoring locations were located to capture spatial distributions of important local pollution sources, and potential topographic modifiers of source and pollutant concentrations. The goal was to capture large industrial point sources (Clairton Coke Works, Edgar Thomson Works, Shenango Coke Works), major roadways, and river valleys across an urban-to-suburban gradient of Allegheny County. A domain of the county was created as a feasible coverage area of 500km^2, extending at least 10km northeast of industrial point sources, with respect to the prevailing west-southwest wind direction [54]. This domain would be used for creation of Pittsburgh exposure surface maps derived from land use regression modeling.

For purposes of sampling site selection, we explored spatial variability across traffic and industrial emission source and modifier (elevation) indicators in GIS. Rivers and riverbanks (<20m from the edge of the river) were removed from the sampling domain. Because traffic-related pollution may vary within 50-200m from roadways [55, 56] and steep elevation gradients are present in Pittsburgh, we used relatively small regular 100m^2 lattice grid cells to characterize the domain according to traffic density, proximity to industrial sources, and topography [54].

Traffic density was calculated as the sum of total vehicle counts on major road segments, plus an estimated 500-vehicle count on minor road segments (sensitivity tested using 250- and 1000-vehicle counts). A kernel density surface was modeled from total traffic counts. The

resulting kernel weighted smooth surface was used to calculate mean traffic density by $100m^2$ grid cell. We opted for this metric over another commonly-used approach where the lengths of major and minor road segments falling within each grid cell are multiplied by vehicle traffic counts and summed. The kernel weighted smooth surface approach minimizes misclassification of cells near, but not intersecting, major roadways (e.g., edge-effects) [54].

Emission-weighted proximity to industrial facilities was calculated by summing EPA NEI emissions from all reporting facilities in Allegheny County, PA for $PM_{2.5}$ (filterable and condensable), nitrogen oxides (NO_X), SO_2, and volatile organic compounds (VOCs) mass in tons [57]. Facility emission totals were inverse-distance weighted (IDW) for each $100m^2$ grid cell centroid, falling within an 80 km radial buffer threshold (and sensitivity tested at multiple distance thresholds), to balance influence of large facilities at the domain edge. We included multiple pollutants in the formulation of this site selection covariate to prevent biasing our sampling design toward one pollutant or industry-type [54].

Because there is no standard metric to determine inversion-prone areas, we opted to use continuous elevation above sea level to maximize spatial resolution, stability over time, and comparability with previous LUR studies [53, 58, 59], and calculated mean elevation within each $100m^2$ grid cell from the U.S. Geological Survey National Elevation Dataset (NED) $30m^2$ resolution raster data set [54, 60, 61]

Sample size was determined by available resources, domain size, logistical limitations, and precedent of 37 monitoring sites for urban LUR modeling [62]. Stratified-random sampling was used to select 31 spatially-distributed monitoring sites across eight exposure strata, using open-source Geospatial Modeling Environment. Six additional monitoring sites were randomly determined to fill spatial gaps in the periphery of the domain, creating a total of 37 distributed

sites. In year two of the study, roughly 33% of distributed sites (n=13) were repeated, and 24 new monitoring sites were selected using the same GIS-based exposure classes and stratified-random approach, in an effort to increase spatial saturation.

1.2.4 Citywide Sampling across 37 Sites

Using GIS, $100m^2$ lattice cells were coded by traffic, elevation, and industry for exposure classifications based on dichotomized covariates, creating 8 unique classes. Across covariates, less intensive exposure classes were designated 1, 10 or 100, while more intensive classes were assigned 2, 20 or 200. A class "111" signifies an expected least emissions intensive cell area that is low in traffic density, at a high elevation, and far from industrial sources. Unique classes do not perfectly capture our continuous covariates, but they are useful for site selection purposes to maximize contrasts. LUR modeling using an extensive set of site-specific covariates is more useful and accurate for deriving exposure estimates across unmonitored locations.

Field teams followed consistent protocols to identify suitable locations (e.g., utility or telephone poles) to mount sampling units near the centroid of selected $100m^2$ grid cells. Mounting pole eligibility criteria included: no obstructions up to 3m radius around the monitors (e.g., signs or wires), street accessible, nine or more feet from buildings, identifiable pole ownership (for permission purposes), not near a bus stop, and no overhanging tree branches. Latitude and longitude coordinates of selected mounting poles were determined using GPS (Colorado 400t, Garmin), and verified in Google Earth. A detailed site survey was conducted for each sampling pole, to document relevant information that may not be available in GIS datasets (e.g., traffic detour or construction). The site survey used for selection of a suitable pole can be found in Appendix B.

Year 1 sampling (summer 2011 and winter 2012) focused on inversion-based hours, which were previously detected in the Braddock mobile monitoring campaign. After discussion of sampling interval, it was determined that the air pollution monitors would sample Monday through Friday from 6 to 11AM. This would capture potential inversion events, as well as the morning rush hour across Pittsburgh. The following two figures show average hourly $PM_{2.5}$ at ACHD monitoring sites during our sampling (Figures 5 and 6). For summer 2011, elevated hourly PM concentrations can be seen during the early morning hours at Liberty; generally, elevated PM concentrations are seen in the 6-8AM hours. For winter 2012, elevated hourly PM concentrations can be seen during our sampling period of 6-11AM.

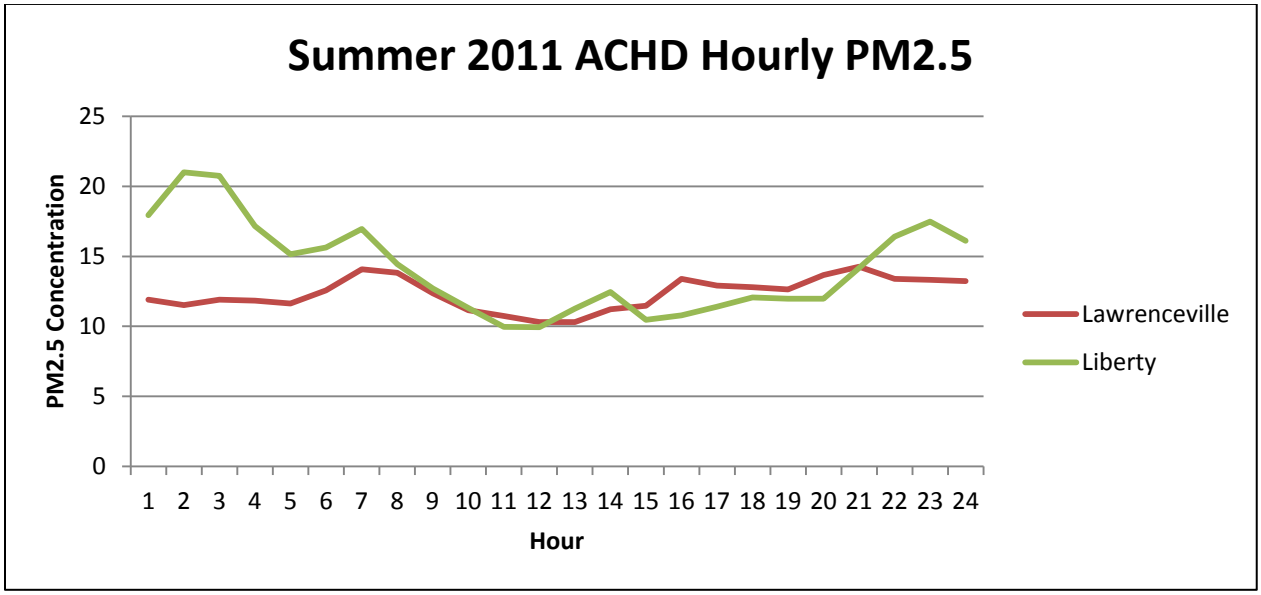


Figure 5. Average hourly $PM_{2.5}$ concentrations at ACHD monitoring sites during the summer 2011 inversion-sampling.

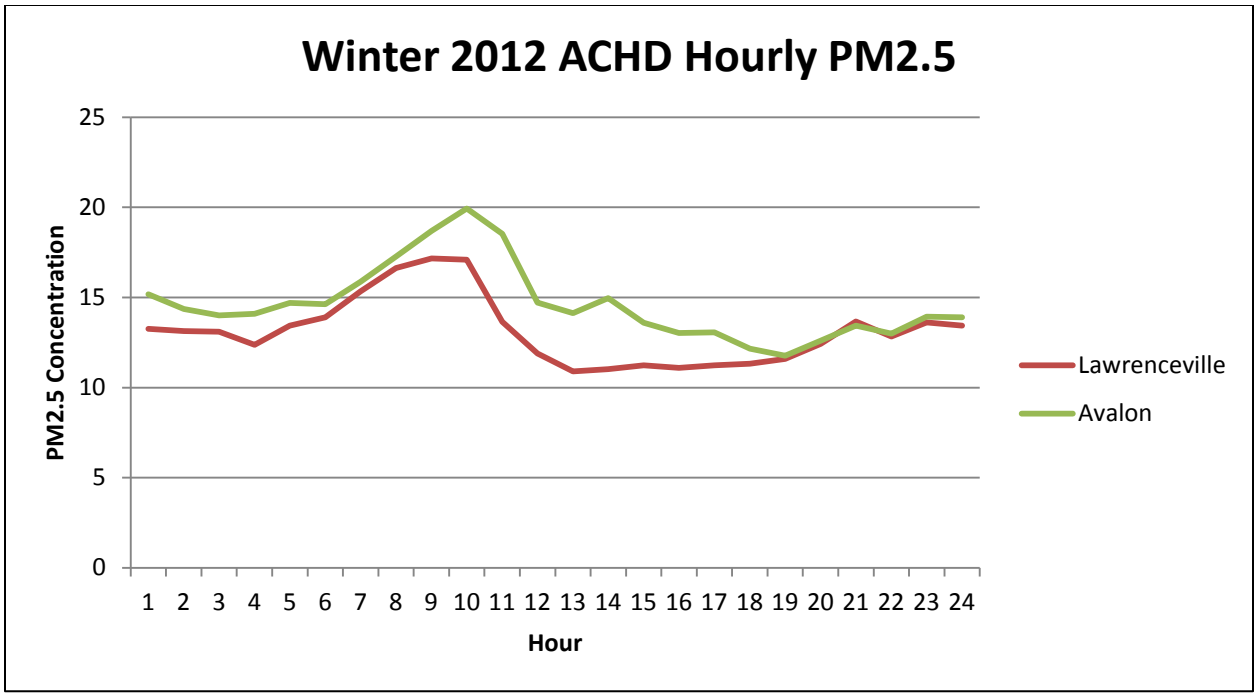


Figure 6. Average hourly $PM_{2.5}$ concentrations at ACHD monitoring sites during the winter 2012 inversion-sampling.

1.2.5 Modeling Pollutant Concentrations to Predict Variability

Land use regression (LUR) models can be developed after establishment of monitoring sites across a designated sampling area of interest and measurement of pollutant levels such as particulate matter and black carbon. The primary use of LUR focuses on predicting pollutant concentrations in areas where monitoring had not taken place. Concentrations at such locations could be estimated after GIS-derived industrial, land use and traffic features are created across a sampling domain. LUR can determine pollution-source relationships, as well as rapid decay of some pollutants [63]. Indicators of particulate matter pollution could be created from various road, traffic, and land type patterns, and these can be assessed as predictors of PM variability using LUR [64].

LUR models are an important tool, allowing for integration of traffic and geographic information to characterize variability in exposures [65]. LUR models can utilize monitored levels of pollutants such as fine particulate matter ($PM_{2.5}$) and black carbon (BC), and then these pollution levels can then be predicted at an unmonitored location using parameter estimates from the regression model [49, 65]. These models, which allow for characterization of exposure differentials within urban areas, may be useful tools in evaluating health effects of long term exposure to pollutants [47, 58]. Further developments of LUR methods include focusing on developing models that can be transferred to other areas [66]. Differences in R^2 from these models may be related to the original variability in measured concentrations and/or the complexity of the city [66]. These models are important for deriving exposure estimates associated with health outcomes; thus, the methodology (i.e. sampling time frame) used for collection of pollutants is important.

LUR models can be built using particulate matter levels at monitored locations (i.e. 37 sites) as the dependent variable and variables such as industrial emissions, land use, and elevation as the independent variables [67]. Pollutant levels can then be predicted at unmonitored locations across the specific sampling domain [52]. For our sampling campaigns in which air pollution monitors were mounted on telephone poles across 37 monitoring locations, LUR models would be developed. This specific number of sites is sufficient for modeling purposes. For LUR, modeling uses measured pollution concentrations y (i.e. $PM_{2.5}$ concentrations) at location s (i.e. 37 distributed monitoring sites) as the response variable, and land use types x within areas (i.e. sum of commercial and industrial parcels) around location s (i.e. 1000 meter buffer) as predictors of the measured concentrations in air [49]. After determining a best-fit final LUR model, smooth surface mapping of pollutant concentrations,

such as $PM_{2.5}$ and BC, can be created via GIS using kriging and kriging with external drift (KED).

Strengths of LUR include low cost, easy implementation, and the construction of regression mapping, allowing for adaption to local areas (such as Pittsburgh) without supplementary monitoring of additional locations [49]. LUR incorporates site-specific covariates, which can be determined via a range of buffer sizes, and it can detect small variations more successfully than other methods [63, 67]. LUR models are better at assessing small-scale variability than kriging (an interpolation model), integrated meteorological-emission models, or dispersion models [49].

For the mobile monitoring study, mixed models were used to seasonally model $PM_{2.5}$ and PM_{10} across a set of 25 stops that were repeated multiple times. Mixed models are statistical models that contain both fixed and random effects. Because the "stops" were repeated many times, these were used as a random effect, as repeated measurements of particulate matter were made. For indoor air sampling, seasonal, pollutant-specific multivariate regression modeling was performed in which the dependent variable was pollutant concentration, and the independent variables included smoking, cooking, other questionnaire covariates, and outdoor spatial covariates such as traffic density and industrial emissions. An outdoor predicted $PM_{2.5}$ and BC concentration was determined using exposure surfaces created from county-wide year one and year two sampling campaigns, and predicted values were incorporated into indoor modeling.

2.0 CHAPTER ONE

2.1 MANUSCRIPT 1: UNDERSTANDING INTRA-NEIGHBORHOOD PATTERNS IN PM2.5 AND PM10 USING MOBILE MONITORING IN BRADDOCK, PA

This manuscript entitled "Understanding intra-neighborhood patterns in $PM_{2.5}$ and PM_{10} using mobile monitoring in Braddock, PA" was published in *Environmental Health* in October 2012. Air pollution from heavy industry has decreased over recent decades, on average, in the United States [26, 68-70]. Nonetheless, a few traditionally industrial communities remain; Braddock, PA, located east of Pittsburgh along the Monongahela River, is one such example. An economically distressed area with high rates of childhood asthma [71], Braddock is home to the Edgar Thomson Steel Works (ETSW), one of the few remaining operational steel mills owned by U.S. Steel in the Pittsburgh area. Pittsburgh became an industrial center when Andrew Carnegie sited the first steel mill along the Monongahela River in 1873. With the decline of steel industry in the early 1980s, Braddock and similar communities lost most of their economic base through layoffs, plant shutdowns, strikes, and workforce reductions [72]. The hilly terrain of the "Mon Valley" region makes measuring the spatial aspect of air pollution particularly important in Braddock.

Braddock is also situated in a federal $PM_{2.5}$ non-attainment area [73]. The 24-hr NAAQS concentration ($35\mu g/m^3$) is typically exceeded on days of high local source emissions and

inversion events, implicating both local and regional contributions. Chu et al. (2009) suggested that local pollution sources, and frequent inversion events in Pittsburgh, are superimposed on a high regional background (owing to proximity to Ohio Valley coal emissions). The extent of $PM_{2.5}$ further varies with sunlight and photochemical processes, temperature, and wind speed and direction from more or less polluted regions [74]. The authors further hypothesized that sources southeast of Pittsburgh strongly influence $PM_{2.5}$ on exceedance days [74], with higher concentrations likely in the source communities. The largest stationary sources of fine particles in Allegheny County lie southeast of the city -- ETSW (8.7 miles from downtown Pittsburgh) and Clairton Coke Works (14.5 miles) [75].

ETSW produced 2.7 million net tons of steel in 2010 (28% of US Steel's domestic production) [76]. In 2008 Toxic Release Inventory (TRI) data, ETSW reported stack air releases of 33,489 lbs., primarily comprised of hydrochloric acid, ethylene, and manganese compounds, and on-site fugitive air releases were 64,849 lb (i.e. sum of EPA Title III compounds) primarily comprised of methanol, ammonia, and zinc [77]. As a part of this mobile monitoring study, we employed Gaussian plume modeling of ETSW emissions, for neutral atmospheric conditions, which indicated centerline $PM_{2.5}$ concentrations up to 60 $\mu g/m^3$ within several kilometers from the plant [78]. This modeling simply provided evidence of the mill contribution to local air pollution and suggested further study in Braddock. Local PM exposures associated with ESTW, however, have not been modeled under an array of local meteorological conditions.

High outdoor air pollution, low socioeconomic status, and African American race, have all been associated with increased asthma prevalence and morbidity [79-83]. The median household income in Braddock was $26,389 in 2010 [72]; approximately 72% of the population is African-American. This confluence of risk factors in Braddock indicates the importance of

better understanding these complex local air pollution exposure patterns, and, ultimately, the contribution of air pollution to local asthma risk [84].

There is one EPA ambient monitoring location in Braddock, at a higher elevation than the plant. One site, however, cannot capture fine-scale spatial variability in this complex region [85, 86], or temporal patterns which may vary across space – either by elevation or by the relative predominance and location of industrial or traffic sources. As such, mobile monitoring may be an informative complement to stationary monitoring -- to better understand temporal and spatio-temporal variability [85, 87] – and to help inform the spatial and temporal design of a fixed-site monitoring network for a complex region.

Mobile monitoring can be built in as a preliminary step of any air pollution field study design because it provides a better representation of local air pollution, providing confidence in placement of stationary air monitors in a neighborhood. Several characteristics of mobile monitoring facilitate its utility as a tool for understanding complex conditions, and, if carefully designed, for disentangling some aspects of temporal and spatial variation. First, mobile monitoring is cost-effective. The route can be customized to focus on particular areas of concern, such as high traffic roads or neighborhood fixed sources. Second, concentrations are typically measured at short intervals using continuous instruments which, with good quality-control efforts, can provide information about short-term peak exposures associated with adverse acute health effects [88]. Therefore, through carefully repeating time- and location-specific measures, this technique adds a level of stability in determining PM concentrations. Third, mobile monitoring can also be used to validate conceptual dispersion models by capturing data at multiple points downwind of the source, under varying wind speed and direction conditions [89, 90]. Finally, leveraging the repeated measures and integrating meteorology and land use

characteristics, mobile monitoring data can be used to more richly characterize spatial variability throughout the region [88], by more knowledgeably tailoring the spatial and temporal characteristics of a fixed-site monitoring network.

To assess intra-community variability in pollution exposures, $PM_{2.5}$ and PM_{10} were collected and analyzed in and around Braddock, PA, during summer 2010 and winter 2011. A mobile monitoring method was repeated along a well-characterized route, to understand the within-neighborhood spatial and temporal variability. It was hypothesized that PM concentrations would vary temporally according to season, time of day, day of week, and wind speed and direction. It was hypothesized that PM concentrations would vary spatially by location, elevation, traffic density, and proximity to local stationary (i.e. ETSW), and mobile sources.

2.1.1 Sampling Design/Route

The sampling route was designed to capture variability in topography, traffic density, and proximity to ETSW. $PM_{2.5}$ and PM_{10} were measured at specified locations along a fixed route of 25 stops using continuous instruments, during multiple weekday mornings and afternoons, in both seasons, at a range of elevations and distances from ETSW. At each location, the vehicle engine was turned off, and monitors allowed to stabilize, to obtain a stable 3- to 5-min mean concentration for each pollutant, before proceeding to the next stop. Each sampling run required approximately 3 hours, during which time meteorological conditions can change significantly; for this reason, stops 1 through 5, sampled at the beginning of each sampling run, were repeated at the end (as stops 21–25).

Two sampling runs were performed through the entire route each week, during either morning or afternoon hours, to capture differing traffic patterns by time of day, and to capture potential inversion hours. Preliminary data analysis revealed, during summer afternoons, significantly less spatial or within-day variability; for this reason, subsequent runs (13–20) focused on morning hours only. In total, 20 runs (15 morning, 5 afternoon) were performed from June 3 to August 20, 2010. Twenty winter sampling runs (10 morning, 10 afternoon) were performed from November 12 to March 1, 2011.

The sampling route began on the Carnegie Mellon University campus location near a large city park, proceeded along a heavily trafficked urban road, and included locations near community spaces (e.g., residences, schools, churches, parks, and commercial areas), as it wound downhill into Braddock (Figure 7). Within Braddock (low-elevation sites), mobile monitoring sites were located along a road with heavy diesel truck traffic, basketball courts, an elementary school, and along the ETSW plant periphery. One designated site was in close proximity to the North Braddock EPA monitoring station, operated by Allegheny County Health Department (ACHD), shown in Figure 7.

The first five stops (5 min duration) were located at higher elevation (277 to 306 m) outside of Braddock. Stops 6 through 20 (3 min duration) were located within the community of Braddock.

Figure 7. The sampling route in Pittsburgh and Braddock, PA.

The Hazdust monitor (Model EPAM-5000, Environmental Devices Corporation (EDC), Plaistow, NH 03865), a light scattering nephelometer for continuous measurements of $PM_{2.5}$ and PM_{10}, was used. The EDC-supplied inlet nozzle for a cut-off of 10 μm aerodynamic diameter for PM_{10} measurements was used. For $PM_{2.5}$, one Hazdust was fitted with an external size-selective

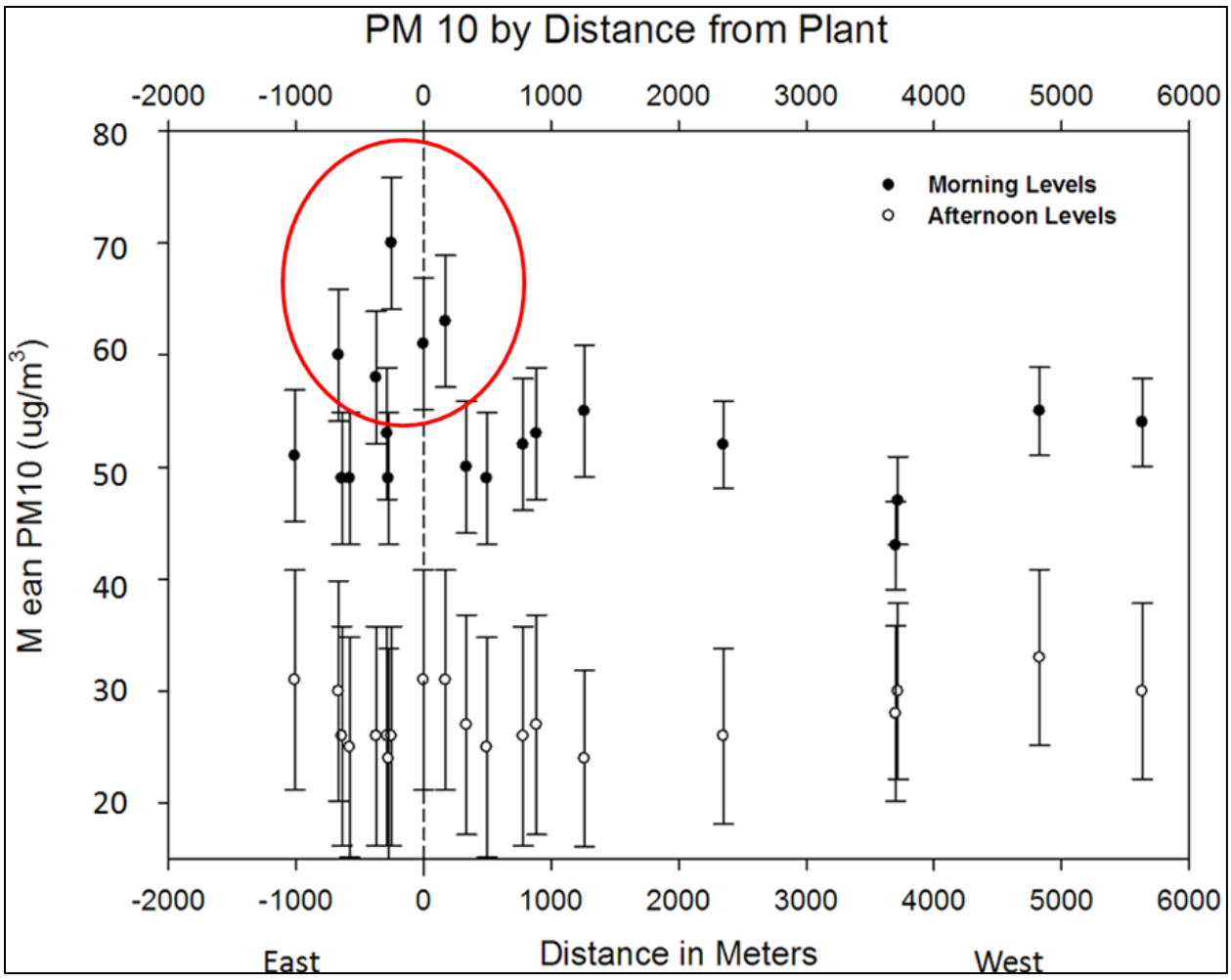
inlet containing a level greased impaction surface with a cut-off of 2.5 μm (aerodynamic diameter). Both Hazdusts were calibrated to operate at 4.0 L/min, and recorded concentrations at 10-s intervals.

The Hazdust monitor automatically purges the sensor optics with clean air, and re-establishes baseline every 30 min. Prior to initiating the study, the Hazdusts were calibrated against gravimetric filter sampling by EDC using an aerosol generator with SAE fine test dust number ISO12103-1 (Arizona Road Dust), and a suite of quality assurance checks were performed. Two $PM_{2.5}$ and two PM_{10} Hazdusts were co-located for one day; PM measures were found to correlate within 5% for each size distribution. Every five sampling runs, the four monitors were again co-located, and no significant change from the initial 5% was observed.

Before each sampling run, one $PM_{2.5}$ and one PM_{10} monitor were secured in the backseat of a passenger vehicle. A 1 m PVC tube with 1.25 cm diameter was attached to each monitor, and the outlet secured 10 to 15 cm outside the rear window, on the passenger side of the car. All monitors were turned on in the parked vehicle with the engine off, and then allowed to operate for at least 20 min, or until readings stabilized, before the vehicle was turned on and the sampling route begun. At the end of this stabilization, baseline values typically ranged from 10 to 20 $\mu g/m^3$ near the loading dock at Carnegie Mellon University (CMU). A standardized log was used to record sampling start and stop times, unusual traffic patterns, precipitation conditions, and limited concentration information. A Colorado 400 t GPS was used to mark each monitoring location, to ensure reproducibility in the precise site locations monitored during each run, and for GIS mapping and analysis.

2.1.2 Particulate Matter Concentrations Near Edgar Thomson Steel Works

During morning sampling, PM_{10} was relatively higher at a cluster of stops near the plant (Stops 11, 12, 13, 14, and 16), indicating near-source spatial variability for PM_{10} (Figure 8). A similar plot for $PM_{2.5}$ indicated no elevated concentrations near the plant.



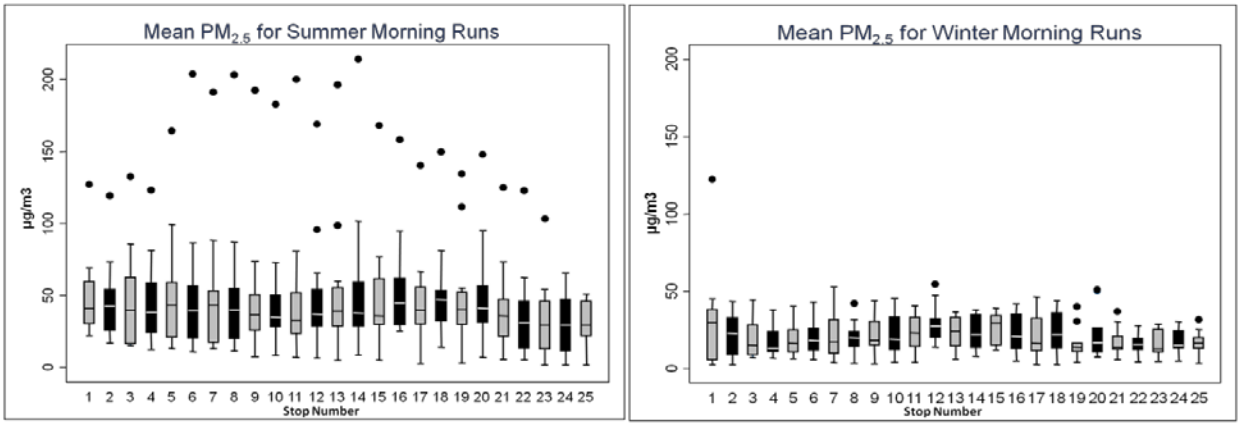
The circled points are likely fugitive emissions or road dust from truck traffic. Stop 12 was used as the distance 0 since it was at the gate of ETSW. Note the clear difference between morning and afternoon runs.

Figure 8. Measured summer PM_{10} concentrations ($\mu g/m^3$) based on distance of stop from the plant

In Braddock, mean $PM_{2.5}$ concentrations at higher elevation (stops 18 and 19) did not significantly differ from concentrations at lower elevations (i.e. along South Braddock Avenue in downtown Braddock). Mean PM_{10}, however, was significantly lower at stops 18 and 19, compared to lower-elevation stops closer to ETSW. $PM_{2.5}$ and PM_{10} concentrations did not significantly correlate with traffic density, either during summer or winter, morning or afternoon sampling ($p > 0.20$ in all cases).

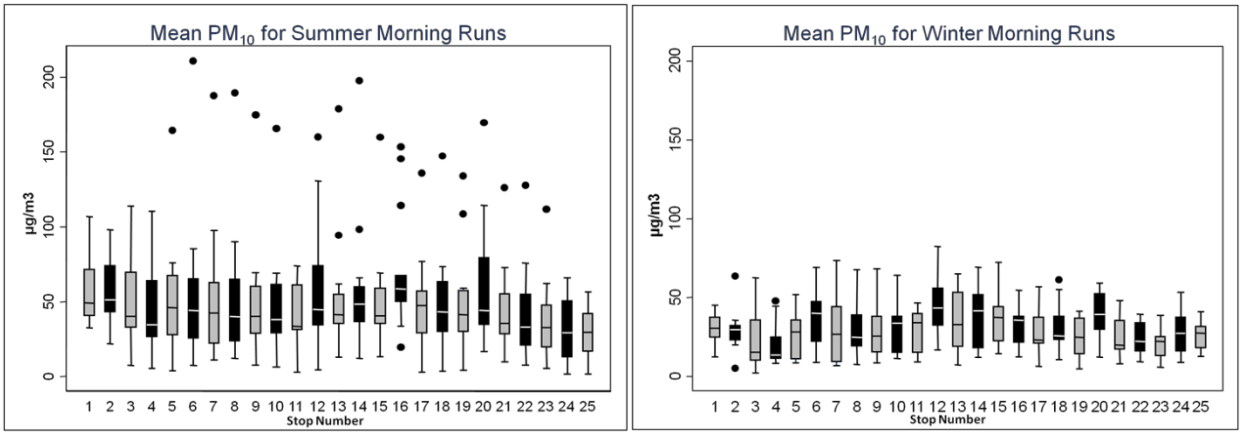
2.1.3 Differences in Seasonal Concentrations: Summer vs. Winter

During summer mornings, mean $PM_{2.5}$ concentrations varied from 30.0 to 55.1 $\mu g/m^3$ (SD = 3.3 and 13.0 $\mu g/m^3$, respectively) across stops. Mean PM_{10} concentrations varied from 30.4 to 69.7 $\mu g/m^3$ (SD = 2.5 and 51.2 $\mu g/m^3$) (Figures 9 and 10).



Note that $PM_{2.5}$ is more variable on summer mornings than on winter mornings.

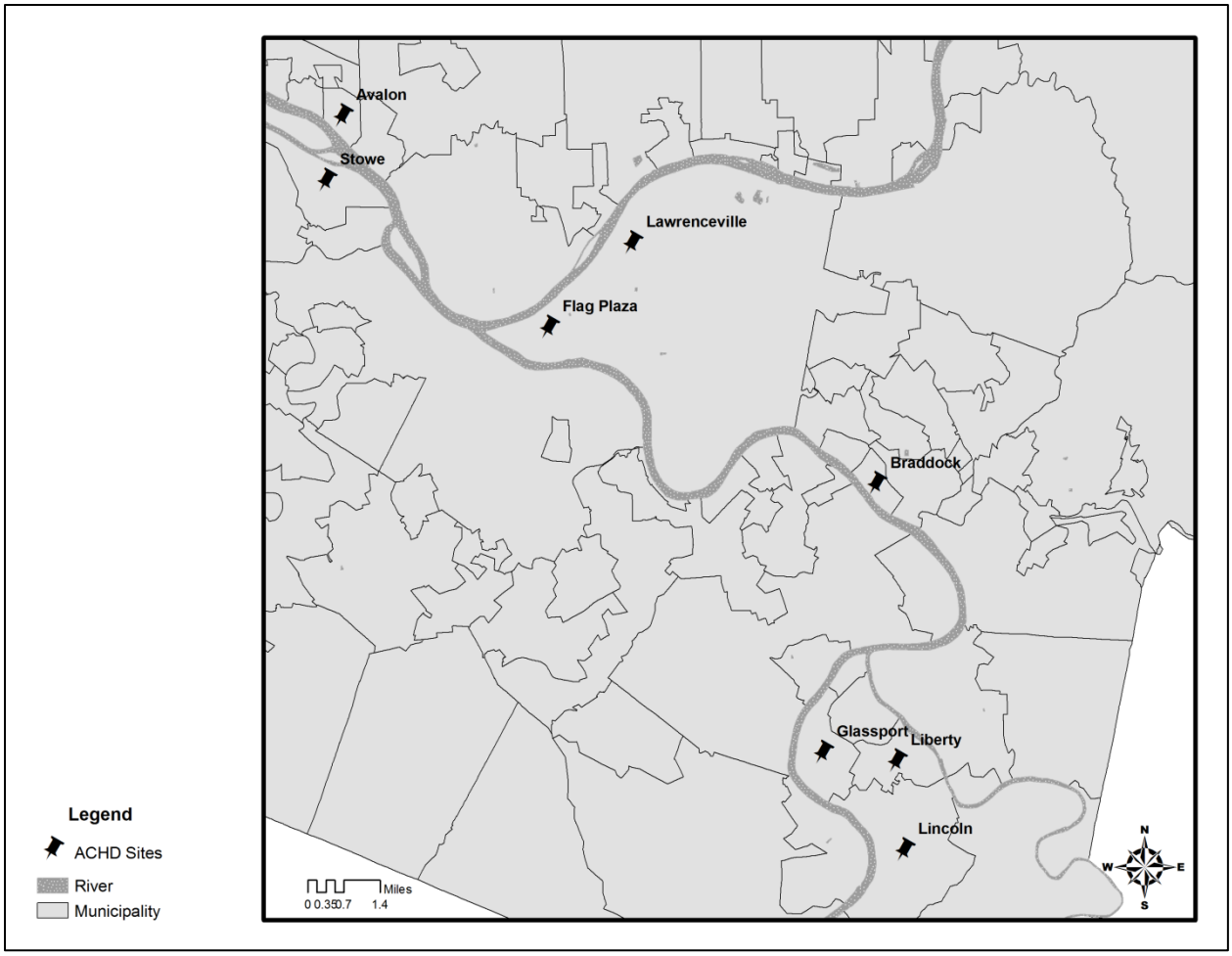
Figure 9. (Left) Mean $PM_{2.5}$ ($\mu g/m^3$) for each stop from 15 summer morning runs; (Right) Mean $PM_{2.5}$ ($\mu g/m^3$) for each stop from 10 winter morning sampling runs.



A mean PM_{10} concentration of 319.1 µg/m3 was omitted for stop 11.

Figure 10. (Left) Mean PM_{10} (µg/m^3) for each stop from the 15 summer morning samplings runs; (Right) Mean PM_{10} (µg/m^3) for each stop on all 10 winter morning sampling runs.

During summer morning sampling hours, our overall mean $PM_{2.5}$ concentration was 46.2 µg/m^3 (SD = 35.7 µg/m^3), approximately twice the average concentration measured at nearby ACHD stationary monitors during the same period (Figure 11). Mean $PM_{2.5}$ at the North Braddock monitor was 29.1 µg/m^3 (SD = 17.9 µg/m^3), 26.9 µg/m^3 (SD = 12.1 µg/m^3) at Avalon (15.0 miles from Braddock), 15.4 µg/m^3 (SD = 8.7 µg/m3) at Lawrenceville (7.6 miles), and 19.9 µg/m^3 (SD = 9.8 µg/m^3) at Liberty (9.0 miles) during the same time period [91].



The North Braddock site in Figures 1,4,5,6 and 7 was the same as the Braddock ACHD site in this figure.

Figure 11. An aerial view of the seven other Allegheny County Health Department (ACHD) monitoring sites throughout Allegheny County in relation to the city of Braddock, PA.

PM_{10} from the mobile monitors, during summer morning sampling, averaged 50.5 $\mu g/m^3$ ($SD = 37.9$ $\mu g/m^3$) overall – again approximately twice the concentrations at local ACHD monitors. PM_{10} was not collected at the North Braddock ACHD site during these hours. At Flag Plaza (downtown, 8.4 miles from Braddock) PM_{10} averaged 26.9 $\mu g/m^3$ ($SD = 11.4$ $\mu g/m^3$), at Glassport (8.4 miles) PM_{10} averaged 26.9 $\mu g/m^3$ ($SD = 15.9$ $\mu g/m^3$), at Liberty 30.0 $\mu g/m^3$

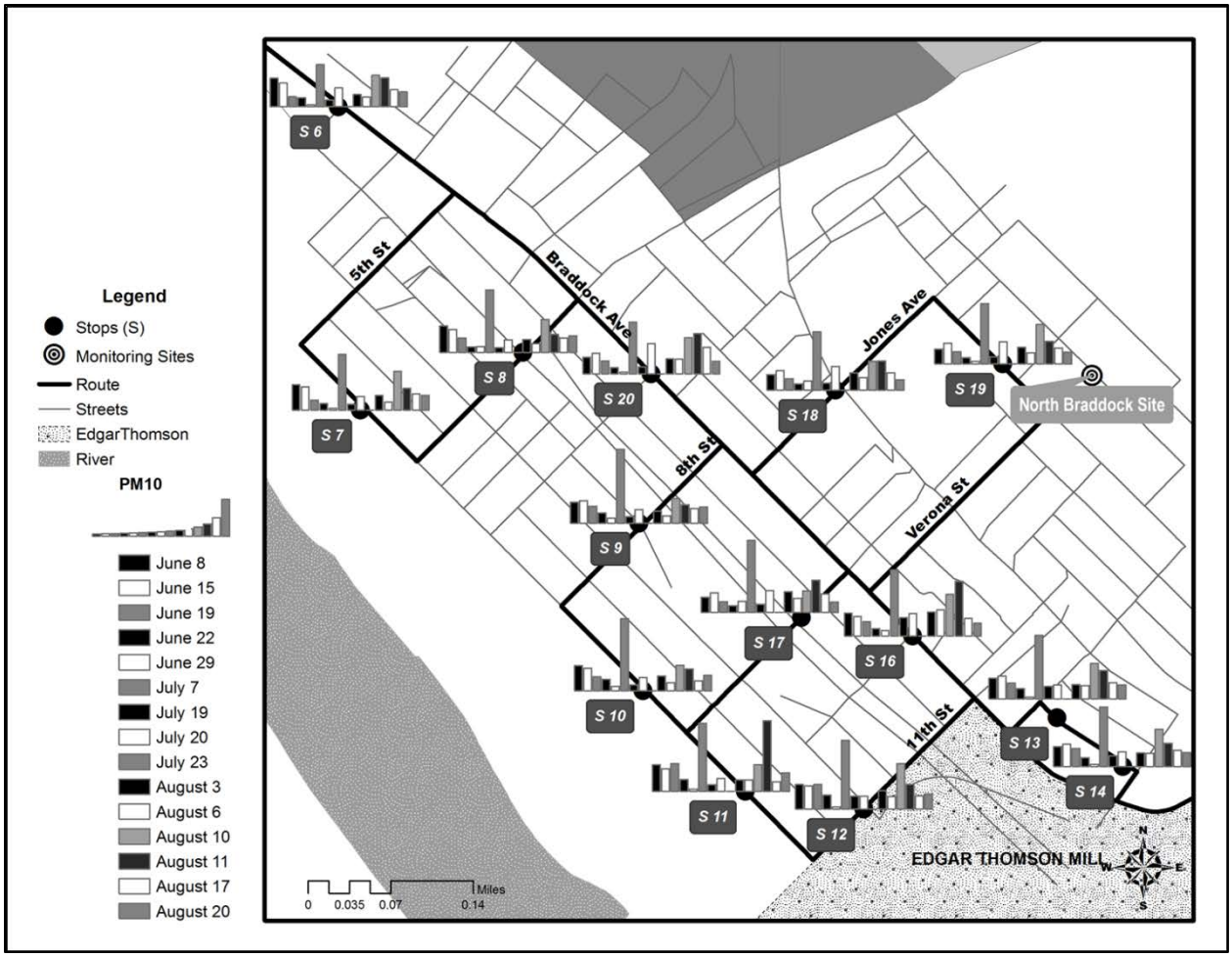
(SD = 13.5 μg/m^3), at Lincoln (12.0 miles) 36.6 μg/m^3 (SD = 17.0 μg/m^3), and at Stowe Township (14.6 miles) 28.8 μg/m^3 (SD = 12.8 μg/m^3).

During winter mobile air sampling, site-specific mean $PM_{2.5}$ concentrations varied from 15.8 to 33.8 μg/m^3 (SD = 2.4 and 11.4 μg/m^3, respectively), and mean PM_{10} varied from 20.0 to 48.2 μg/m^3 (SD = 2.6 and 22.5 μg/m^3, respectively). For both $PM_{2.5}$ and PM_{10}, winter concentrations were significantly lower than summer ($p < 0.0001$). The $PM_{2.5}$ to PM_{10} ratio was consistently above 0.6 during winter sampling.

During winter, morning $PM_{2.5}$ and PM_{10} concentrations were higher than afternoon, though the AM to PM difference was smaller than for summer. Mean mobile winter morning $PM_{2.5}$ was 21.6 μg/m^3 (SD = 13.5 μg/m^3), but no ambient data for comparison were reported at the North Braddock monitoring site during these periods. Mean PM_{10} mobile data were 30.4 μg/m^3 (SD = 16.5 μg/m^3), somewhat higher than the mean ambient PM_{10} concentration of 25.9 μg/m^3 (SD = 13.4 μg/m^3).

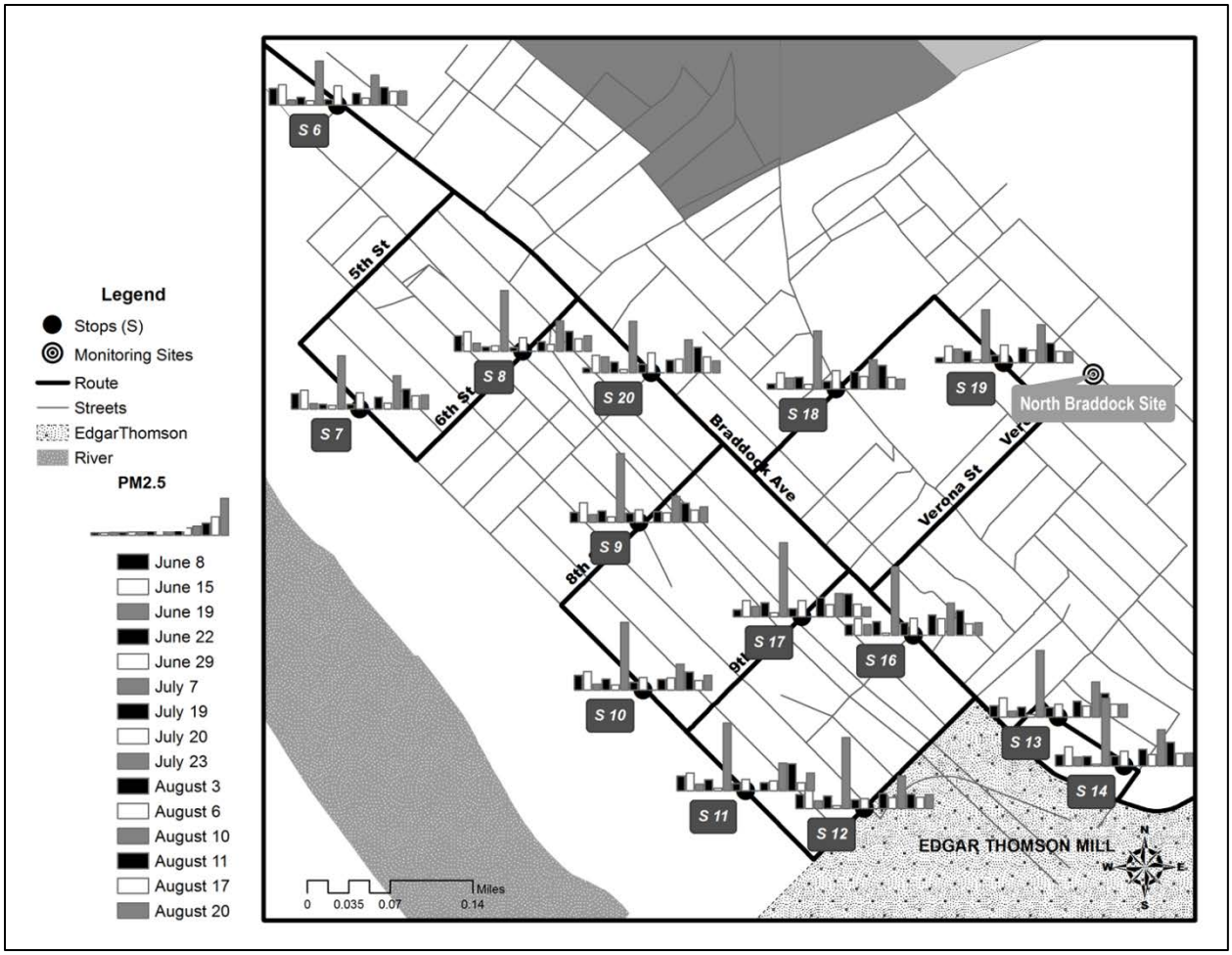
2.1.4 Spatial and Temporal Variability in Concentrations

$PM_{2.5}$ and PM_{10} mobile monitoring data depict substantial temporal variation across sampling days, and some spatial variation between stops (Figures 12-14).



The bar height refers to the average daily PM_{10} concentration ($\mu g/m^3$) at each stop.

Figure 12. The stops and sampled concentrations of PM_{10} in downtown Braddock, PA for morning runs in the summer 2010.



The bar height refers to the average daily $PM_{2.5}$ concentration ($\mu g/m^3$) at each stop.

Figure 13. The stops and sampled concentrations of $PM_{2.5}$ in downtown Braddock, PA for morning runs in the summer 2010.

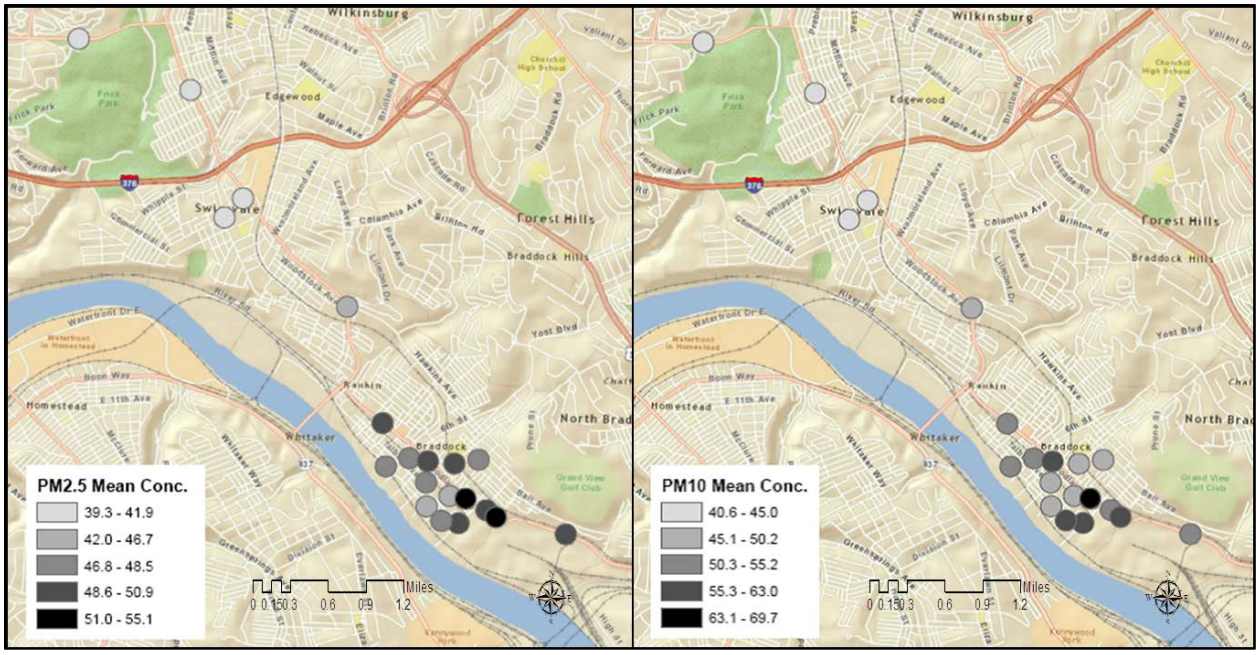


Figure 14. Spatial variability of morning summer mean $PM_{2.5}$ (left) and PM_{10} (right) concentrations ($\mu g/m^3$) across all stops.

To assess the effect of temporal variation during each sampling period, five stops were sampled at both the beginning and end of each run, labeled as stops 1–5 and 25–21, respectively. Pairwise comparison of these repeated stops suggests a significant temporal effect during summer morning sampling, with lower concentrations of both $PM_{2.5}$ and PM_{10} later in the morning ($p < 0.029$); repeated stops did not significantly differ in the winter ($p > 0.169$).

In bivariate analysis, wind speed was positively correlated with $PM_{2.5}$ concentrations during both summer and winter mornings, and PM_{10} concentrations during the summer ($p < 0.05$). Wind direction also significantly affected concentrations; higher $PM_{2.5}$ were observed during periods when winds blow towards the north or northeast, and lower concentrations when winds blow towards the south or southwest, relative to periods of westerly winds. For PM_{10}, concentrations were significantly higher during periods of non-westerly winds, with lower concentrations only with winds towards the south.

2.1.5 Presence of Inversion Events

During summer months, afternoon mobile sampling concentrations were significantly lower than morning concentrations, for both $PM_{2.5}$ and PM_{10} ($p < 0.0001$). The $PM_{2.5}$ to PM_{10} ratio, during both morning and afternoon sampling, was typically above 0.8. Using BUFKIT, atmospheric inversions were identified during 50% of summer morning sampling periods. No inversion events were detected during summer afternoons or the winter sampling season. Accordingly, higher PM was observed during summer mornings than afternoons.

On July 7, an inversion event that contributed to a photochemical smog occurred in and around the Pittsburgh area, during a morning sampling run. Mean $PM_{2.5}$ measured between 46.2 and 214.3 (SD = 10.7) $\mu g/m^3$ across all stops, and mean PM_{10} measured between 42.4 and 319.1 (SD = 31.1) $\mu g/m^3$. During this period, elevated PM_{10} concentrations were noted at the local ambient monitors: Glassport (58.4 $\mu g/m^3$ (SD = 32.7 $\mu g/m^3$)), Lincoln (61.8 $\mu g/m^3$ (SD = 32.4 $\mu g/m^3$)), Liberty (55 $\mu g/m^3$ (SD = 28.2 $\mu g/m^3$)), and Stowe Township (52.8 $\mu g/m^3$ (SD = 42.2 $\mu g/m^3$)).

2.1.6 Building Multivariate Linear Regression Models

Wind speed and direction data were obtained from the ACHD Air Quality Monitoring Station in Liberty, PA at South Allegheny High School (4.9 miles South of Braddock). Bufkit 10.11, a forecast profile visualization and analysis tool kit developed by the National Oceanic and Atmospheric Association (NOAA) and National Weather Service, was used to identify local atmospheric inversions during sampling hours, per instructions of NOAA personnel (John Darnley, personal communication). Models embedded in Bufkit include the Rapid Update Cycle

(RUC), North American Mesoscale Model (NAM) and Global Forecast System (GFS). The RUC model updates once each hour, with a 1-h lag behind the latest model runs. The NAM and GFS Bufkit profiles update four times daily (0, 6, 12, and 18 h) with an approximate 2-h lag.

An indicator of traffic density around each sampling stop was created using ESRI ArcInfo Version 10 (Redlands, CA). Roadway shapefiles for Allegheny County were obtained from Pennsylvania Department of Transportation's (PENNDOT) publicly available annualized average daily vehicle-count data for primary roadways. At each stop, 100-m buffers were constructed in ArcInfo, and the length of primary and secondary roads (in feet) within the buffer was calculated using open-source Geospatial Modeling Environment (Spatial Ecology LLC). Roadway lengths were multiplied by average daily traffic counts, and summed to estimate a total traffic density covariate within 100 m buffers around each of the 25 mobile monitoring stops. For secondary roads, where traffic counts were unavailable, an estimated daily volume of 500 vehicles was applied to create another covariate for our analysis. This was based on a minimum primary road count of approximately 3600 vehicles and sensitivity testing for secondary road count estimates at 100, 250, and 1000 vehicles. Sensitivity testing for buffer size around each stop varied from 100–500 m. Sampling stops were sufficiently close together that buffers larger than 100 m overlapped, reducing apparent variability between the stops.

To evaluate the influence of topography and relative distance to ETSW, spatial covariates describing "distance to mill" and "elevation" were created using ESRI ArcInfo (version 10). Elevation above sea level was assessed as point intersection with the National Oceanographic and Atmospheric Digital Elevation Model, varying from 224 to 306 m at each of the designated stops. Using the 1996 Pennsylvania Digital Elevation Model – 10 m layer, these elevation values were calculated from the Coincident Point method using the Spatial Join tool in the Analysis

Toolset [92]. Using the 2008 Allegheny County TRI Emission Points dataset, ETSW was geocoded, and distance to mill was measured as Euclidean distance between each stop and the entrance to the ETSW using the Geoprocessing Proximity Toolset 'Near' tool, varying between 0 to 5,633 m, with stop 12 (at entrance to the mill) designated as 0 m from ETSW [57]. ETSW was the "nearest" large source to all of the 25 designated stops.

Descriptive statistics, scatterplots, and histograms were used to characterize distributions of $PM_{2.5}$ and PM_{10} concentrations, spatial covariates (traffic density, elevation, distance to mill) and temporal covariates (temperature, relative humidity, wind speed and direction) (Table 1). Prior to model-building, mean $PM_{2.5}$ and PM_{10} were examined in bivariate analysis against each continuous independent variable, and between high and low categories for binary and median-dichotomized source covariates. Data analysis and model-building was performed separately for $PM_{2.5}$ and PM_{10}, and for summer and winter, using only morning data (~7 am to ~10 am).

Table 1. Descriptive statistics for mobile monitoring morning versus afternoon.

	Summer		**Winter**	
	Morning	*Afternoon*	*Morning*	*Afternoon*
Mean $PM_{2.5}$ ($\mu g/m^3$)	46.2 (S.D. 35.7)	29.1 (S.D. 20.1)	21.6 (S.D. 13.5)	15.5 (S.D. 12.7)
Mean PM_{10} ($\mu g/m^3$)	50.5 (S.D. 37.9)	27.7 (S.D. 21.2)	30.4 (S.D. 16.5)	24.8 (S.D. 21.8)
Temperature (Mean, Min, Max °F)	70.9 (58 – 80)	78.2 (68-90)	23.1 (8-50)	35.8 (17-65)
Relative Humidity (Mean, Min, Max %)	75.1 (30-92)	54 (37-71)	75.9 (60-93)	57.5 (16-88)
Wind Speed (Mean, Min, Max mph)	5.8 (2.9-10.4)	7.7 (6.4-10.4)	5.7 (2.9-10.4)	9.1 (2.9-16.2)

*Wind direction: Summer: 30% SW, 25% W, 15% N, 10% NW, 10% S, 5% E, 5% NE
Winter: 35% W, 20% SW, 15% NW, 15% NE, 10% S, 5% E

**Elevation varied from 224 to 306 meters.

***Traffic density indicators varied from 595,668 to 19,961,739 based on GIS calculations around each stop (Refer to methods).
****Distance to mill varied from 0 to 5,633 meters.

Multiple linear regression models were built sequentially, using a manual forward-stepwise model building procedure. Covariates significant at $p < 0.05$ in bivariate analysis were individually incorporated, ordered by strength of the bivariate correlation. Model fit was assessed at each stage, using the coefficient of determination (R^2), p-value, and parameter estimate (β). At each stage, non-significant covariates were individually removed in order of descending p-value, and the model re-fit. After all significant main effects were identified and incorporated, an interaction term between wind speed and direction was examined. Statistical analyses were conducted using Proc Reg and Proc GLM in SAS version 9.3 (SAS Institute Inc., Cary, NC) and Stata version 11 (StataCorp, LP, College Station, TX). Figures were produced using Stata 11 and SigmaPlot 10 (San Jose, CA).

Scatterplots were examined to assess the fit between each significant predictor and PM concentrations, to ensure that covariate selection was robust, and not reliant on outlier source values. Likewise, the fit of each additional term was tested against the residual of the prior model in the sequential model-building process. Stop order was incorporated, as both an integer and categorical covariate, to identify residual within-day variance not accounted for by other temporal and meteorological covariates. Model residuals were examined to ensure normality, and compared predicted $PM_{2.5}$ and PM_{10} to observed concentrations and examined model fit through scatter plots. To assess model sensitivity to the effect of repeated measures by stop, final source covariates from the linear regression model were used to construct a one-level mixed effects model with random effects (intercept and slope) by stop. In all cases, selected covariates

retained significance, and contributed to model fit, according to Akaike information criterion (AIC).

Pearson correlations between covariates and PM concentrations were determined. During summer mornings, $PM_{2.5}$ was predominantly explained by meteorology – temperature, wind speed, wind direction, and the interaction of wind speed and direction (Temporal Seq $R^2 = 0.73$, Spatial $R^2 = 0.002$) (Table 2). Higher temperatures conferred lower concentrations, after adjusting for all other model terms; each additional degree F was associated with a decrease of about 2 $\mu g/m^3$ in $PM_{2.5}$ (a major reason for mixing height is temperature). Higher wind speeds, on average, were associated with higher $PM_{2.5}$, though this effect was strongly modified by wind direction; higher concentrations were observed with winds from the north or northeast (from direction of mill or Ohio Valley, respectively), and lower concentrations with winds from the south or southwest. Distance to mill was the only spatial covariate that explained additional (marginal) variability in $PM_{2.5}$ during summer mornings; $PM_{2.5}$ was 0.145 $\mu g/m^3$ lower, on average, for each 100 m distance from the mill. Overall model fit was strong, explaining approximately 74% of the variability in $PM_{2.5}$ concentrations.

For summer mornings, PM_{10} was also predominantly explained by meteorology, including terms for wind speed, wind direction, inversion events, and an interaction between wind speed and direction (Temporal Seq $R^2 = 0.62$, Spatial $R^2 = 0.01$) (Table 2). Notably, both wind speed and direction had similar influences on PM_{10} as on $PM_{2.5}$. PM_{10} was 0.220 $\mu g/m^3$ lower, on average, with each 100 m distance from the mill. The presence of inversions accounted for an increase of 13.6 $\mu g/m^3$, on average, in PM_{10}. Overall model fit was strong, explaining approximately 64% of the variability in PM_{10} concentrations. The models for winter sampling

were similar to summer models (explaining 51 to 54% of variability in PM), as meteorology was the primary contributor and elevation replaced distance from the mill.

In sensitivity testing, final model results were robust to the effects of outliers and repeated measures by stop. All model covariates retained significance regardless of other terms retained in each model, and contributed to model fit, according to Akaike information criterion (AIC). Stop order was incorporated as a sensitivity analysis, to identify additional within-day variance not captured by temporal or meteorological terms, but did not improve model fit.

Table 2. Final mixed model covariates and model fits for summer morning $PM_{2.5}$ and $PM_{10.}$

		Mixed Model		
Summer Morning $PM_{2.5}$ ($\mu g/m^3$)	**Covariates**	β (SE)	p-value	Seq R^2*
	Intercept	102.63 (16.364)	<.0001	--
	Temperature (°F)	-1.99 (0.297)	<.0001	0.15
	Wind speed (mph)	21.83 (2.120)	<.0001	0.27
	Wind direction:		<.0001	0.58
	E	23.885 (3.435)	<.0001	--
	N	158.33 (12.284)	<.0001	--
	NE	109.09 (5.199)	<.0001	--
	NW	8.406 (3.154)	0.0080	--
	S	-48.763 (12.322)	<.0001	--
	SW	-115.40 (11.904)	<.0001	--
	W	0	--	--
	Distance to mill (m)	-0.00145 (.00034)	<.0001	0.59
	Wind speed x Wind direction:	--	<.0001	**0.74**
	N	-39.674 (3.112)	<.0001	--
	S	6.264 (2.625)	0.0176	--
Summer Morning PM_{10} ($\mu g/m^3$)	Intercept	-37.949 (8.932)	0.0066	--
	Wind speed (mph)	23.896 (2.683)	<.0001	0.17
	Wind direction:		<.0001	0.46
	E	32.833 (5.476)	<.0001	--
	N	110.52 (10.786)	<.0001	--
	NE	80.831 (5.590)	<.0001	--
	NW	2.866 (4.377)	0.5130	--

Table 2 Continued

	S	-29.902 (8.534)	<.0001	--
	SW	-135.66 (16.140)	<.0001	--
	W	0	--	--
	Distance to mill (m)	-0.0022 (.0005)	<.0001	0.48
	Inversion presence	13.634 (2.960)	<.0001	0.53
	Wind speed x Wind direction:	--	<.0001	**0.64**
	N	-30.397 (2.960)	<.0001	--

*Seq R^2 is the sequential model fit for each additional term incorporated into model.

Table 3. Final mixed model covariates and model fits for winter morning $PM_{2.5}$ and $PM_{10.}$

		Mixed Model		
	Covariate description	β (SE)	p-value	Seq R^2
Winter Morning $PM_{2.5}$ ($\mu g/m^3$)	Intercept	5.899 (8.038)	0.4637	--
	Temperature (°F)	-1.959 (0.340)	<.0001	0.25
	Wind speed (mph)	6.750 (1.169)	<.0001	0.25
	Wind direction:		<.0001	0.42
	E	87.865 (12.151)	<.0001	--
	NE	42.795 (7.964)	<.0001	--
	NW	49.339 (9.593)	<.0001	--
	S	-121.40 (18.543)	<.0001	--
	SW	52.125 (9.358)	<.0001	--
	W	0	--	--
	Elevation (m)	-0.0695 (0.0194)	0.0004	0.44
	Wind speed x Wind direction:	--	<.0001	**0.54**
	S	24.015 (3.425)	<.0001	--
Winter Morning PM_{10} ($\mu g/m^3$)	Intercept	-0.551 (12.470)	0.9648	--
	Temperature (°F)	-4.154 (0.473)	<.0001	0.16
	Wind speed (mph)	13.498 (1.717)	<.0001	0.16
	Wind direction:		<.0001	0.26
	E	159.50 (17.417)	<.0001	--
	NE	97.496 (11.835)	<.0001	--
	NW	110.48 (13.984)	<.0001	--
	S	-226.06 (26.480)	<.0001	--

Table 3 Continued

	SW	120.93 (13.672)	<.0001	--
	W	0	--	--
	Elevation (m)	-0.135	<.0001	0.31
	Wind speed x Wind direction:	--	<.0001	**0.51**
	S	46.058 (4.805)	<.0001	--

2.1.7 Why Use Mobile Monitoring?

Measurements of $PM_{2.5}$ and PM_{10} concentrations in and around Braddock, PA, during summer and winter months 2010–2011, highlight the impact of summer morning inversion events on particulate pollution. PM concentrations showed a temporal pattern, but were relatively spatially homogenous for our sampling routes. Large temporal variation was observed in short term measured $PM_{2.5}$ and PM_{10} across multiple sampling days, including higher $PM_{2.5}$ and PM_{10} concentrations in summer vs. winter and morning vs. afternoon. These findings provide a better understanding of the spatial and temporal variability of PM in Braddock, and provided critical information about appropriate sampling windows for future monitoring.

During summer, patterns were observed between morning and afternoon PM concentrations. The PM ratio was above 0.8 for summer sampling, suggesting fresh fine plant-related particle emissions e.g. furnace and trucks, in contrast to re-suspension at the sampling sites; the PM ratio was above 0.6 for winter sampling, and salt spread on the street may have contributed to re-suspended PM [93, 94]. Data on this PM ratio are sparse, and the National Resources Defense Council (NRDC) relies on the generally accepted assumption that this ratio in United States cities is typically 60% [95]. Though most influence appeared to be from fine particles, the main influence of PM_{10} occurred in areas directly adjacent to the plant facilities

during the morning. Distance to the mill was a significant covariate in the summer sampling session (Table 2). Further, the decline of PM_{10} as one moved away from the plant into the community was an important spatial result for the future stationary monitoring campaign throughout Braddock. The spatially-created traffic variables were insignificant in the regression modeling, in which all of the stops were incorporated. However, when comparing a stop that was repeated the same day over a time differential of approximately 3 hours, significant differences were seen in PM concentration and traffic may be a contributor to those changes.

The current study demonstrated that spatial and temporal relationships need to be determined in a first step to adequately characterize exposure of individuals living and working in the Braddock area. These findings are an important aid to having a better understanding of the pattern of air pollution exposures around Braddock, PA, which may have important public health and policy repercussions [96, 97].

Factors that were important to consider in this study include topography (i.e. elevation) and local atmospheric inversions. Elevation was a significant covariate for the winter sampling session. Fine PM in this urban area was also influenced by proximity to the steel mill, transient emission events, and measurement error [98]. During a temperature inversion, the air becomes stagnant, and the valley walls trap air pollution near the surface. Inversion was included for the summer morning PM_{10} model, but dropped out of significance for the $PM_{2.5}$ model when the wind interaction term was incorporated (Table 2). For summer sampling, stops 21 to 25 typically recorded $PM_{2.5}$ and PM_{10} concentrations lower than those measured at stops 1 to 5. It is likely that the observed variations are due to changes in the influences of sources. Chu et al. (2009) reported that sources to the south and southeast of the Pittsburgh Supersite significantly influenced $PM_{2.5}$. Sources located in other directions from the monitoring site had less influence

despite greater emissions and a high frequency of winds. Building on Chu et al. (2009), we examined the role of wind. In assessing our multiple linear regression models, wind direction appeared to be the strongest covariate for the summer and winter months. Winds have been shown to play important roles in transport of pollutants, such as photochemical transport from New York City into Connecticut [99]. Wind speed was positively correlated with $PM_{2.5}$ concentrations during both summer and winter mornings, even though wind speed is generally negatively correlated with air pollutants. However, since the meteorology is measured at an away location in Liberty, PA, local perturbations due to dilution of primary particles from the sources could have been masked by area sources. Chu et al. (2010) demonstrated that high temperatures and relative humidity in the eastern United States may be associated with high $PM_{2.5}$ concentrations to a greater extent than elevated concentrations of SO_2 or O_3 or high levels of UV [100]. An association with relative humidity (RH) was not found, but an inverse relationship with temperature (higher temperatures resulted in lower PM) was found in models (Table 2). One possibility for higher PM in the summer could be power plant emissions, but more likely in the eastern US it is a higher baseline caused by secondary aerosols formed by photochemical smog. Higher temperatures would break up an inversion which would be a main consideration for local sources; recall that the sampling was keyed to time of day, and not simply the 24 h average.

A strength of the mobile monitoring approach is that it allowed us to construct multiple snapshots of spatial and temporal variability in air pollution in areas immediately adjacent to mobile or stationary sources relatively quickly and inexpensively. It also provided a detailed morning versus afternoon pattern in PM concentrations for the summer months 2010, and suggested that fresh combustion and particle re-suspension may be the primary sources for PM

pollution in and around Braddock. In contrast to prior mobile monitoring studies, we instituted a practice to account for session temporal variability by re-sampling the same stops at the beginning and end of the route. A criticism of many studies that aim to discover a relationship between air pollution and health is that exposure is typically characterized using measurements from a few sparsely located air quality monitoring stations, and often only one [101]. Mobile monitoring has been used to characterize spatial variability in black carbon concentrations for land use regression, even though it conventionally requires long-term measurements at multiple locations [88]. Conversely, our mobile monitoring approach provided a more detailed interpretation of the spatial and temporal 'exposure surface' throughout Braddock. Using our models, the correlation between predicted and measured mean PM concentrations varied from 0.70 to 0.88 (highest observed in summer morning $PM_{2.5}$).

Because the mobile monitoring devices are handheld, cost-effective (e.g. multiple samples with high frequency and mobility), and can provide real-time PM or VOC measurements, there is a possibility that communities could deploy these units after a training program conducted by skilled exposure or air pollution scientists [102, 103]. Active neighborhood sampling could make residents aware of air pollution levels, and individuals could actively investigate areas where they feel that pollution levels are too high. By following a time- and location-specific approach, communities could collect a significant amount of repeated measures data to get a sense of the pollution where they reside, and address the occurrence of high pollution events. Therefore, mobile monitoring could be investigated for use in community based participatory research (CBPR) to provide neighborhood residents with the opportunity to proactively investigate potential air pollution. However, interpretation of the results will still require skilled professional analysis.

While the mobile monitoring data provided valuable information, one limitation is that a sampling interval of 3 to 5 min is too short to provide an accurate exposure profile for Braddock residents; these data primarily allow us to gain an understanding of patterns of exposure, and future research can then examine an association to asthma. Although ETSW operates year round, specific plant activity data would have been important in explaining the temporal variation between sampling days, but data was not available for analyses. Future monitoring will include sites with a more complete contrast in source proximity, elevation, and density of traffic, with a specific interest in morning sampling (6 AM to 11 AM), and a design that results from this study, to observe potential effects of inversion events on air pollution concentrations across the Pittsburgh region. A technological limitation is that the Hazdust EPAM-5000 is calibrated using "Arizona road dust" (EDC, Plaistow, New Hampshire -personal communication), which is not representative of Pittsburgh-area aerosols. For this reason, comparisons were provided between our data and ACHD (FRM) measurements in Pittsburgh. However, it is difficult to calibrate any continuous monitor with the local aerosol since one would have to collect and resuspend such material, which would change its basic character and size distribution.

This approach provided the foundation for the design of a longer-term air pollution monitoring strategy for Braddock and the city of Pittsburgh. Based on results from this study, city-wide sampling will be performed Monday through Friday during potential morning inversion hours (6 to 11 AM) using eight stationary monitors (two reference monitors, six distributed monitors), randomized and spatially re-allocated each week, over six weeks each season, to estimate $PM_{2.5}$ in concentrations capturing the range of elevation, proximity to industry, and traffic density across the Pittsburgh metropolitan area.

3.0 CHAPTER TWO

3.1 MANUSCRIPT 2: SPATIAL VARIATION IN INVERSION-FOCUSED VS. 24-HOUR INTEGRATED SAMPLES OF $PM_{2.5}$ AND BLACK CARBON ACROSS PITTSBURGH, PA

Land use regression (LUR) models are an important tool for urban spatial exposure assessment, allowing for integration of traffic and geographic information to characterize variability in exposures [65]. LUR models can utilize monitored levels of pollutants such as fine particulate matter ($PM_{2.5}$) and black carbon (BC); pollution levels can then be predicted at an unmonitored location using parameter estimates from the regression model [49, 65]. These models allow for characterization of concentration differentials within urban areas and may be useful in evaluating health disparities and effects of long term exposure to pollutants [47, 58]. LUR-derived air pollution measures are well-suited for source-apportionment, which provides important info for understanding health mechanisms and policy interventions. Particulate matter constituent factor analysis can determine source contributions to measured $PM_{2.5}$ concentrations, and apportionment methods have linked specific health effects to groups of PM components and sources [47, 104, 105]. Further developments of LUR methods include more focus on creation of models that can be transferred to other areas [106]. Since these models are important for deriving exposure estimates for health outcomes, the sampling methodology should be well

developed, including the sampling intervals (e.g., morning versus afternoon, 24-hr integrated, continuous hours) used for collection of pollutants to determine an exposure surface across the area of interest.

An emphasis on inversion-focused periods of sampling could result in high spatial exposure contrasts across an urban area such as Pittsburgh. Most LUR's have used passive samplers, which are low-cost and deployed across many locations simultaneously. More recent LURs have used active sampling and multi-pollutant approaches, often reducing the number of samples taken concurrently. In this study, active, timed samples were used to capture specific hours of interest and explore spatial variation during hypothesized hours of peak spatial contrast.

Countywide spatial variability in air pollution concentrations can vary due to proximity to industrial sources, traffic density, and other site characteristics such as population and land use, and can also be modified by elevation and meteorological factors [47]. Pittsburgh, PA is characterized by complex terrain, periods of heavy traffic, large industrial sources of pollution, and frequent inversion events [107]. This combination of topography, meteorology, and specific emission sources can result in significant spatial variability in fine particulate matter ($PM_{2.5}$) and black carbon (BC) concentrations. Although industrial air pollution has decreased over recent decades in the United States, remaining steel mills and coke works southeast of Pittsburgh (Edgar Thomson Steel Works and Clairton Coke Works) are large stationary sources of fine particles in Allegheny County, resulting in federal $PM_{2.5}$ non-attainment [68, 70, 75, 108]. The combination of hills and river valleys, episodes of traffic congestion, and large legacy industrial sources causes Pittsburgh to rank as one of the most polluted cities for $PM_{2.5}$ pollution both in daily and annual concentrations [109]; therefore, Pittsburgh is an ideal area to develop spatial saturation methodology to explore unique source and topography profiles. Improved

understanding of spatial variability in air pollution in Pittsburgh could provide insight into air quality in other urban areas with complex topography and industrial sources.

Previous research identified frequent morning inversion events in the Pittsburgh industrial suburb of Braddock [107]. Regulatory monitors within the county have exceeded both the average annual (>12 $\mu g/m^3$) and daily (>35 $\mu g/m^3$) National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$ [108]. In Pittsburgh, high $PM_{2.5}$ levels could be attributable to inversion events occurring in the river valleys, in which both local industrial and traffic emissions become trapped. Inversion events occur when the normal vertical temperature gradient is inverted, causing pollutants to become trapped near ground level, most commonly during morning hours before the inversion layer is dispersed. This trapping of pollutants is of concern to public health since particulate matter and black carbon have been linked to respiratory and cardiovascular diseases [22, 50, 68, 110]. Inversion events can lead to heightened spatial contrasts in pollutant concentrations; therefore this study adjusted sampling time accordingly, and included potential inversion effect modifying factors to capture these events.

Using Geographic Information Systems (GIS), 37 sampling locations across Allegheny County, including the city of Pittsburgh, were systematically selected based on traffic density, industrial emissions, and elevation for summer and winter sampling of $PM_{2.5}$ and BC over a two year period. Year 1 sampling occurred from 6-11AM Monday through Friday hours selected to maximize the frequency of atmospheric inversions, whereas year 2 sampling occurred for a seven day, 24-hour integrated period. Seasonal and pollutant-specific LUR modeling was applied for exposure assessment to characterize intra-urban variability in air pollution concentrations and pollution source apportionment, and smooth surface pollutant-specific exposure maps were created [46, 47, 111].

This study employed a series of stationary monitoring campaigns to characterize intra-urban variability, to compare sampling methodology between the years of sampling, and to create exposure surface maps across Pittsburgh [112]. It was hypothesized that inversion-focused sampling would reveal stronger spatial contrasts across the Pittsburgh domain and stronger impacts of local emissions sources distributed in LUR models. It was also hypothesized that variability in pollutant concentrations would be predicted by measures of traffic density, summed industrial emissions, elevation change, and the frequency of inversions. A citywide sampling design allowed for exploration of mean variation in $PM_{2.5}$ and BC concentrations based on spatial, seasonal, and temporal differences. The study was anticipated to capture variation in $PM_{2.5}$ and BC concentrations by elevation, proximity to industry, traffic density, and inversion events using a sampling interval designed to capture heightened spatial contrasts and stronger source signatures.

3.1.1 Sampling Design and GIS-Based Methods (Traffic, Elevation, Industry)

For more information on sampling site allocation and classification, refer to Shmool et al. [113]. GIS-based methods were used to quantify spatial distributions of local pollution sources (e.g., proximity to industry and traffic) and potential modifiers (e.g., elevation). Sampling locations (n=37) were allocated to capture spatial and source variability (e.g., stratified random sample) across the Pittsburgh metropolitan area (~150 sq. miles). Regular $100m^2$ lattice cells were assigned using a specific classification system based on traffic density, industrial emissions, and elevation. Emission indicators were cross-stratified to capture differing combinations (Figure 15). Sampling methodology and design for year 2 was similar to year 1 inversion-based

sampling, and one-third of the sites from year 1 sampling were repeated during year 2 sampling for direct comparison [113].

For year 1 (inversion-focused monitoring), each 5-day (Monday through Friday) sampling session included deployment of air pollution samplers which collected $PM_{2.5}$ from 6-11AM at six distributed and one reference site. The reference site used throughout the sampling season to assess regional background pollution was at Settlers Cabin Park in Carnegie, PA. An additional urban reference site in Braddock was sampled every session. A total of six sampling sessions were performed during summer 2011 from July 25 to September 9, 2011 with one week skipped due to logistical delay. Sessions were repeated for winter 2012 from January 16 to February 24, 2012. For year 2 (24-hour integrated monitoring), sampling methods were similar to year 1 methods aside from sampling duration which was adjusted to an integrated 24-hour 7-day sample. Year 2 sampling was performed in summer 2012 (June 5th to July 26th) and repeated in winter 2013 (January 8th to March 10th). A total of eight sites were sampled per session for better temporal adjustment, and due to equipment availability, sampling schemes were performed during separate years.

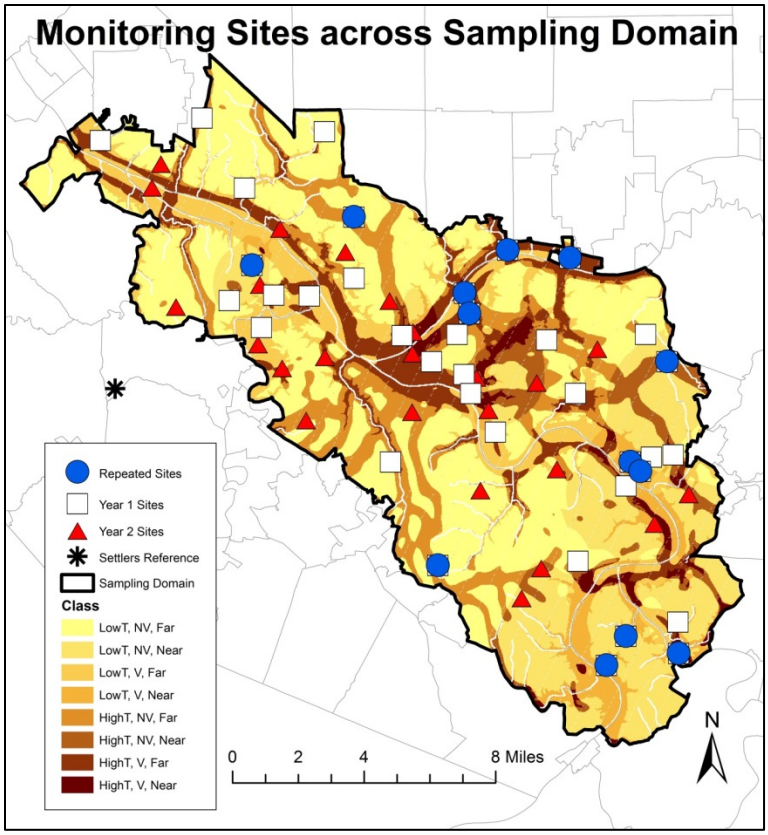


Figure 15. Domain of Allegheny County stratified according to classification system with monitoring sites.

Using a temperature (20°C) and relative humidity (35%) controlled glove box (PlasLabs Model 890 THC), 37mm Teflon filters (Pall Life Sciences) were equilibrated for 48 hours and then pre-weighed using an ultramicrobalance (Mettler Toledo Model XP2U) before deployment at monitoring locations. After collection of the samplers, the filters were then post-weighed under the same conditions. Sampling units were custom-designed to capture integrated street-level samples of $PM_{2.5}$ [38]. Sampling instruments, including Harvard Impactors (Air Diagnostics and Engineering Inc.) with 37mm Teflon filters and a HOBO data logger (Onset Computer Corporation), were contained in waterproof Pelican cases. Instruments were programmed for specific hours of sampling using a chrontroller (ChronTrol Corporation). A

tetraCal volumetric air flow calibrator (BGI Instruments) was used to calibrate the flow to approximately 4.0 LPM. The HOBO data logger recorded temperature and relative humidity at fifteen minute intervals at each sampling site. Black carbon was measured (in absorbance units) from each filter using an EEL43M Smokestain Reflectometer (Diffusion Systems).

GIS-based covariates were calculated across a range of source indicator categories (Table 4). All analyses were conducted using ESRI ArcInfo Version 10 (Redlands, CA), and all covariates summarized for monitoring locations and multiple buffers. Roadway shapefiles for Allegheny County were obtained from Pennsylvania Department of Transportation's (PennDOT) publicly available annualized average daily vehicle-count data for primary roadways. Traffic covariates included mean kernel density, sum of signaled intersections, mean density of bus and truck traffic, summed length of roadway (in feet), and total traffic density (vehicle count). Point elevation at each monitoring location, as well as the average elevation within multiple radial buffers (50 to 1000 meters) was assessed, using the National Oceanographic and Atmospheric Digital Elevation Model [60, 61]. For industrial emissions, $PM_{2.5}$ (filterable and condensable), nitrogen oxides (NO_x), sulfur dioxide (SO_2), and volatile organic chemicals (VOCs) were aggregated from the USEPA's 2011 National Emissions Inventory (NEI) [114]. Inverse distance weighting interpolation was used, and summed pollutant values were determined. The summed density of total Toxic Release Inventory (TRI) emissions (in pounds) was also determined. Land use covariates were created in which the total area of industrial and the combination of commercial and industrial parcels were summed. The distance from and summed line length of active railroad was also assessed. Census data were obtained at block group level, and population was assessed [115].

Table 4. GIS-based source density indicators used for LUR modeling.

Source category for LUR Modeling	Covariates examined (50m to 1000m buffers)	Data source
Traffic density indicators	Mean density traffic (primary roads) Mean density traffic (primary and secondary roads) Number of signaled intersections	Pennsylvania Department of Transportation (PADOT)
Road-specific measures	Average daily traffic on nearest primary road Distance to nearest major road Summed length of primary roadways Summed length of primary and secondary Roadways	PADOT
Truck, Bus, and Diesel	Mean density of bus traffic Distance to nearest bus route Outbound and inbound trip frequency per week summed by route Mean density of heavy truck traffic on nearest primary roadway	Google Transit (11/11 -3/12) PADOT
Population	Census population density (blockgroup)	US Census Bureau (2010)
Land Use / Built Environment	Total area of industrial parcels Total area of commercial parcels Total area of industrial and commercial parcels Percent developed imperviousness	Allegheny County Assessment Data, by parcel (2011) National Land Cover Dataset (NLCD, 2006)
Industrial emissions	Summed density of total TRI pounds emitted per meter Summed density of total NEI pounds of $PM_{2.5}$, SO_2, NOx, and VOCs emitted per meter Summed density of total $PM_{2.5}$ emitted per meter Summed density of total SO_2 emitted per meter Summed density of total NOx emitted per meter Summed density of total VOCs emitted per meter	EPA Toxics Release Inventory (TRI, 2010) National Emissions Inventory (NEI, 2011)
Transportation Facilities	Distance to nearest active railroad Summed line length of active railroads Distance to nearest bus depot	Southwestern Pennsylvania Commission (SPC, 2011)
Potential Modifying Factors		
Topography	Average elevation	National Elevation Dataset (NED, 2011)
Meteorology	Temperature/Relative Humidity Frequency of Inversions Wind Direction and Wind Speed	Obtained from sampler Univ. of Wyoming, Dept. of Atm. Science (2011-2012) National Oceanic and Atmospheric Association (NOAA, 2011-2012)

Atmospheric sounding data (i.e., Skew-T diagrams) were used to identify the presence of temperature inversions during 6-11AM sampling hours (year 1), and the 24-hour integrated hours (year 2) [116]. A binary inversion metric was created in which every day of sampling was determined to have an inversion or not. Wind speeds and wind directions were cropped according to the 6-11AM Monday through Friday sampling scheme or the 24-hour integrated 7-day sampling duration [117]. Environmental soundings and wind data were recorded at the Pittsburgh International Airport, approximately 15 miles northwest of downtown Pittsburgh.

The $PM_{2.5}$ and BC concentrations at the distributed monitoring sites were temporally adjusted for both years of sampling, using the background reference site. To make temporal adjustments, the $PM_{2.5}$ concentration at a particular monitoring location was divided by the specific weekly $PM_{2.5}$ concentration from the background reference site and then multiplied by the overall seasonal average $PM_{2.5}$ concentration determined at the background reference site.

An additional seventh monitoring session for each season was incorporated to co-locate monitors at four randomly selected sites for quality assurance purposes. Field blanks were used during each session of the study, and the entire set of filters was blank-corrected. Hourly $PM_{2.5}$ concentrations were obtained from Allegheny County Health Department (personal communication with Allason Holt) for the Liberty, Lawrenceville, and Avalon monitoring locations. The data were then aggregated to specific hours in which $PM_{2.5}$ was sampled (6-11AM Monday through Friday or 24-hour integrated 7 day). These locations were used as additional reference sites to compare to our background and urban reference sites for quality reassurance purposes.

3.1.2 Spatial and Temporal Variability in PM2.5 and Black Carbon

The temporally adjusted mean $PM_{2.5}$ concentration for year 1 summer sampling was 14.35 $\mu g/m^3$ (SD=3.97), and mean BC absorbance was 1.64 abs (SD=0.91) (Figure 16). Inversions were detected 1 to 3 days per session. During year 1 winter, a temporally adjusted mean concentration of 12.76 $\mu g/m^3$ (SD=2.57) for $PM_{2.5}$ was measured. Mean BC absorbance was 1.34 abs (SD=0.53) (Figure 16). Inversions were detected 2 to 4 days per session.

The temporally adjusted mean $PM_{2.5}$ concentration for year 2 summer sampling was 13.94 $\mu g/m^3$ (SD=2.01), and mean BC absorbance was 1.70 abs (SD=0.58) (Figure 17). $PM_{2.5}$ concentrations were on average lower than those found in year 1 summer monitoring, whereas BC absorbance in year 2 was higher (Table 5). During year 2 winter sampling, a temporally adjusted mean $PM_{2.5}$ concentration of 11.26 $\mu g/m^3$ (SD=2.01) was measured, and the mean BC absorbance was 1.54 abs (SD=0.58) (Figure 17). $PM_{2.5}$ concentrations were on average lower compared to those found in year 1 winter monitoring, whereas BC absorbance in year 2 winter was higher (Table 5).

A subset (n=13) of monitoring sites were sampled both year 1 and year 2 for direct comparability. Average mean $PM_{2.5}$ concentrations from these repeated sites in summer year 1 were 14.88 (SD=5.04) $\mu g/m^3$, whereas 14.42 (SD=2.96) $\mu g/m^3$ for summer year 2. For winter year 1, mean $PM_{2.5}$ was 13.74 (SD=3.37) $\mu g/m^3$, while winter year 2 concentrations were 11.49 (SD=2.66) $\mu g/m^3$. Higher $PM_{2.5}$ concentrations were found throughout year 1 inversion-focused sampling compared to year 2 24-hour integrated sampling. For summer, 62% (8 of 13) sites had lower concentrations in year 2, and for the winter, 77% (10 of 13) sites had lower concentrations in year 2. The correlation between $PM_{2.5}$ concentrations of repeated sites between years was 0.56 for the summer and 0.24 for winter. Concentrations remained similar at the background reference site for both seasons (summer year 2= 11.92 (SD=3.99) vs. summer year 1= 11.91 (SD=2.22; winter year 2= 8.43 (SD=1.76) vs. winter year 1= 8.64 (SD=1.73)).

For summer year 1, mean BC was 1.63 (SD=1.03) abs, whereas for summer year 2, mean BC was 1.91 (SD=0.79) abs. For winter year 1, mean BC was 1.43 (SD=0.67) abs, whereas for winter year 2, mean BC was 1.67 (SD=0.72) abs. On average, higher BC absorbance was found during year 2 sampling at the repeated sites compared to year 1. For summer, 62% (8 of 13)

sites had higher absorbance in year 2, and for the winter, 92% (12 of 13) sites had higher absorbance in year 2. The correlation between BC absorbance of repeated sites between years was 0.62 for the summer and 0.80 for the winter. Mean BC absorbance was higher during year 2 sampling (summer year 2=1.03 (SD=0.18) vs. summer year 1= 0.77 (SD=0.11); winter year 2= 0.89 (SD=0.33) vs. winter year 1= 0.62 (SD=0.03)) at the background reference site.

Table 5. Descriptive statistics for citywide air sampling concentrations and meteorology.

	Summer 2011	**Winter 2012**	**Summer 2012**	**Winter 2013**
Mean $PM_{2.5}$ ($\mu g/m^3$)	14.35 (±3.97)	12.76 (±2.97)	13.94 (±2.01)	11.26 (±2.01)
Mean BC (abs)	1.64 (±0.91)	1.34 (±0.53)	1.70 (±0.58)	1.54 (±0.58)
Temperature (Mean, Min, Max °F)	69.26 (61.9-78.1)	34.07 (19.8-40.7)	76.99 (70.0-82.0)	34.07 (25.1-44.5)
Relative Humidity (Mean, Min, Max %)	85.85 (75.5-98.7)	78.55 (69.5-87.7)	61.59 (46.2-79.2)	72.19 (55.3-85.2)
Wind Speed (Mean, Min, Max m/s)	1.79 (1.3-2.2)	3.20 (2.3-3.9)	2.66 (2.2-3.5)	4.21 (3.2-5.0)
Wind Direction (% of sessions)	33% W, 33% SW, 17% SE, 17% NE	50% SW, 33% W, 17% N	33% NW, 33% SW, 17% W, 17% S	33% NW, 33% W, 33% SW
Inversion Presence (% of sessions)	50% 2 inversions 33% 3 inversions 17% 1 inversion	50% 3 inversions 33% 4 inversions 17% 2 inversions		

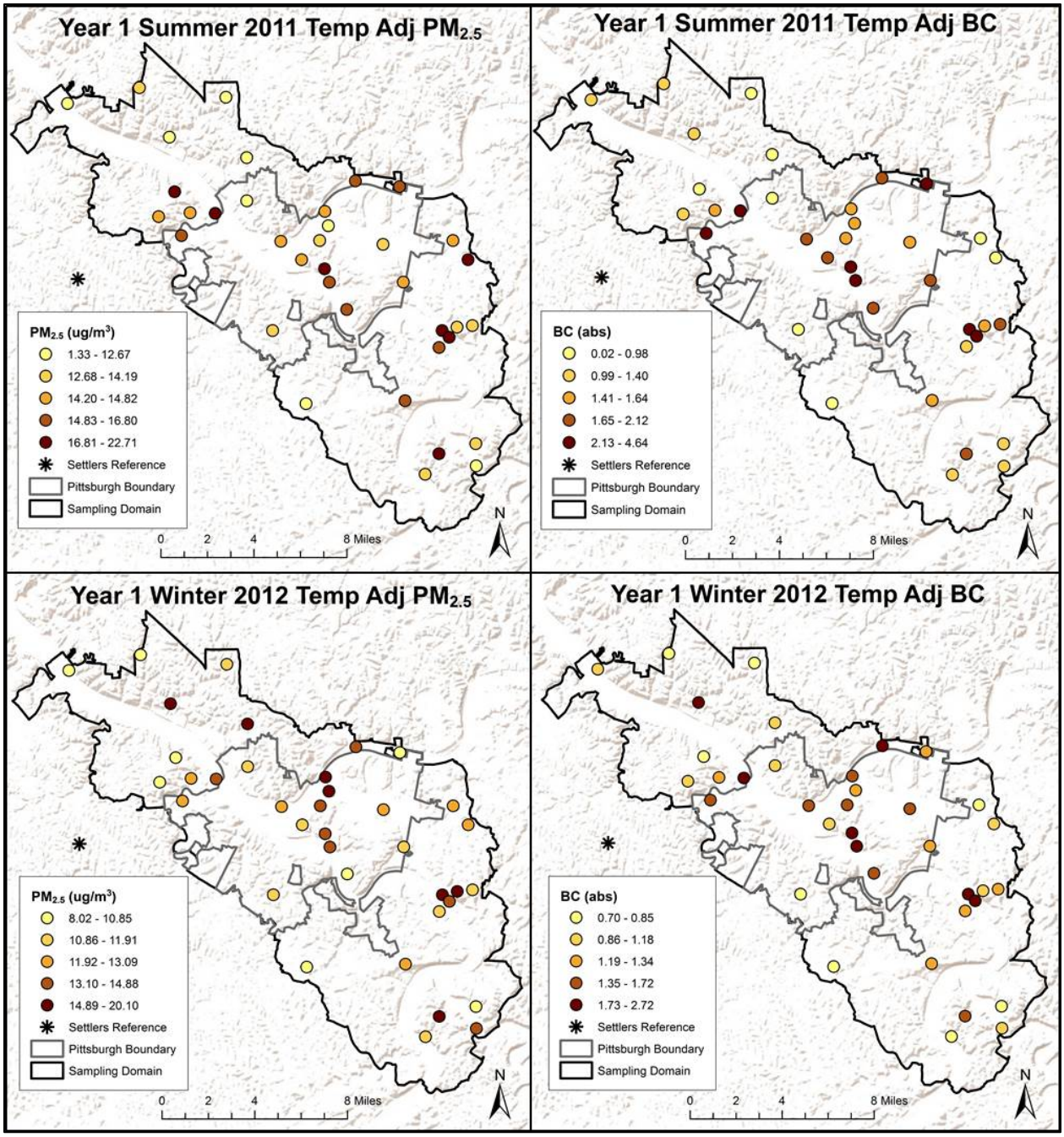


Figure 16. Year 1 summer and winter $PM_{2.5}$ and BC monitoring data depict spatial variability across sites.

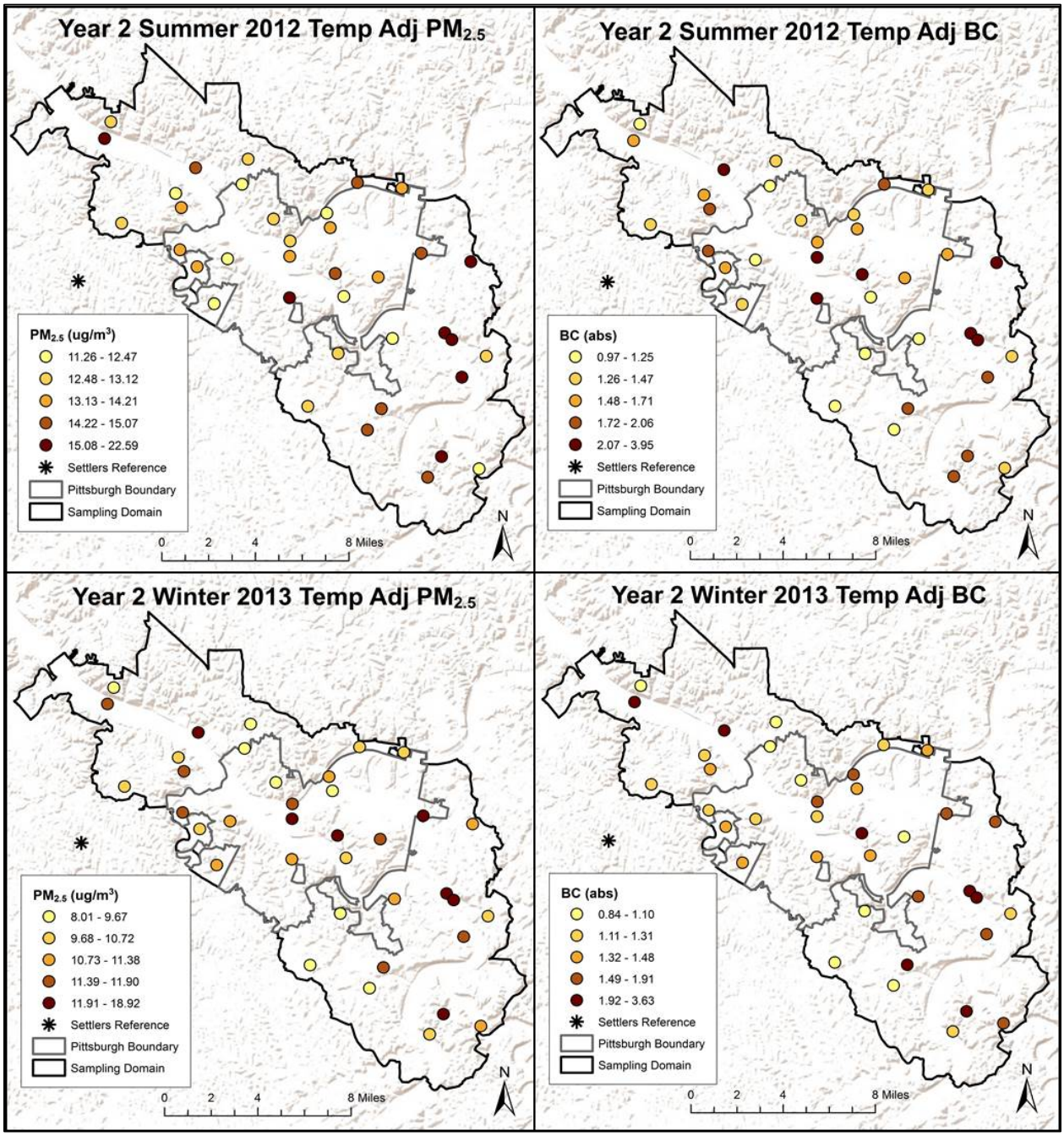


Figure 17. Year 2 summer and winter $PM_{2.5}$ and BC monitoring data depict spatial variability across sites.

Strong temporal trends at the two sampling reference sites (Braddock and Settlers), as well as Allegheny County Health Department (ACHD) sites (n=2 for year 1, n=4 for year 2), can be seen in summer and winter sampling (Figure 18).

For both years, wind direction was predominantly from the west, and wind speeds were generally higher during winter sampling hours compared to the summer (Figure 19).

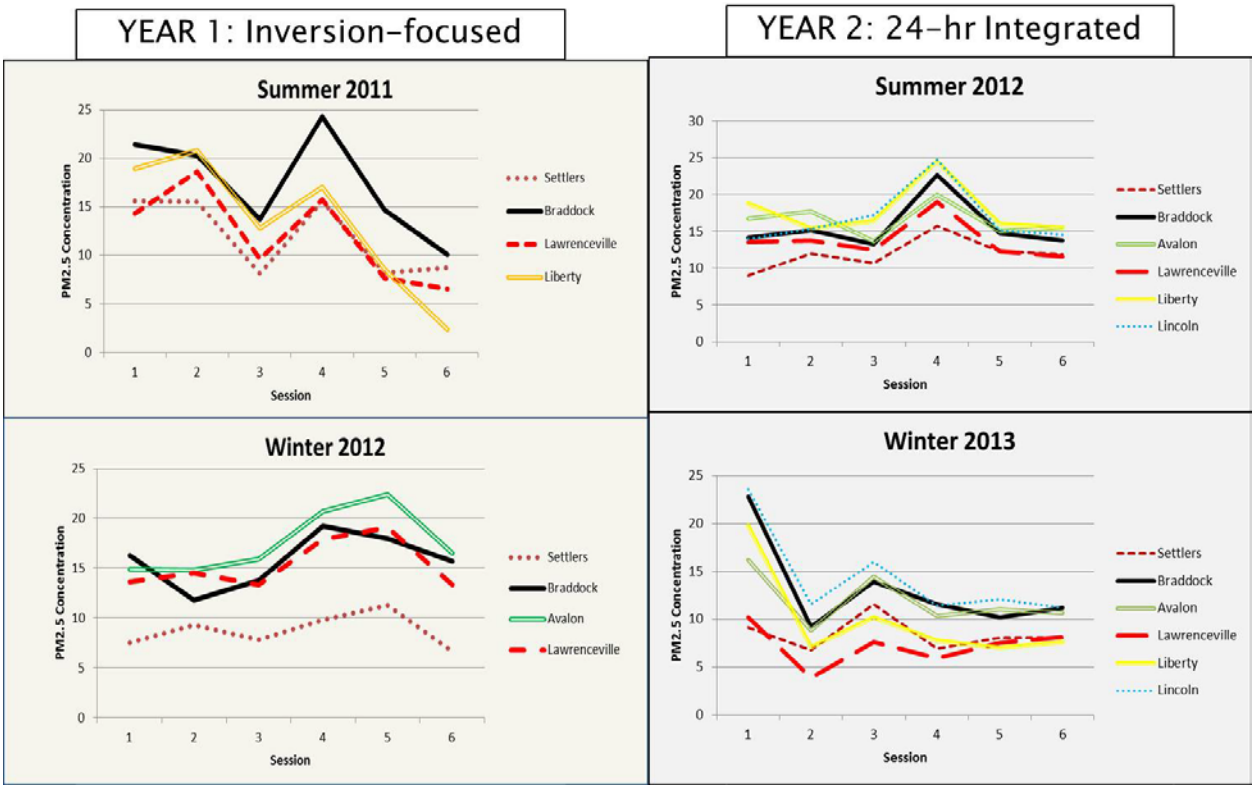


Figure 18. Temporal trends across sampling reference sites.

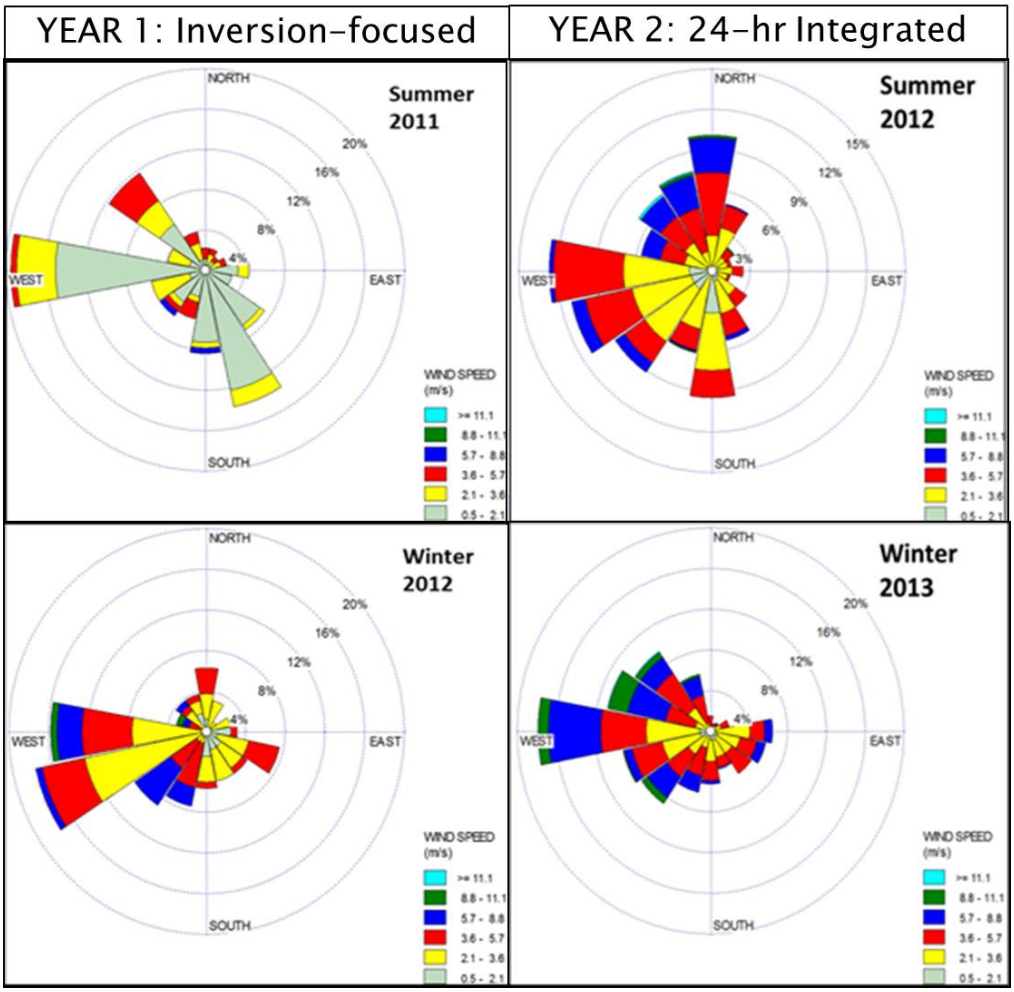


Figure 19. Wind rose diagrams across all hours of sampling.

3.1.3 Building Pollutant-Specific LUR Models

Descriptive statistics, scatterplots, and histograms were used to characterize distributions of $PM_{2.5}$ concentrations and BC absorbance values, spatial ArcInfo covariates (e.g. traffic density, elevation, industrial emissions) and temporal covariates (temperature, relative humidity, wind speed, wind direction, frequency of inversions) (Table 5). Before modeling, bivariate analyses of pollutants with independent variables were performed. Data analysis and model-building was performed separately for $PM_{2.5}$ and BC and for summer and winter seasons.

Statistical analyses were conducted using Proc GLM in SAS version 9.3 (SAS Institute Inc., Cary, NC).

LUR models were implemented using manual forward step-wise linear regression, to assess $PM_{2.5}$ and BC concentrations for the summer and winter seasons. The full set of source indicator covariates (Table 4) were modeled separately for each pollutant and each season. First, bivariate correlation coefficients (Spearman rho) were examined, and the two most significant covariates from each source category were individually incorporated, ordered by strength of the bivariate correlation. The temporal trends in $PM_{2.5}$ and BC were first incorporated into LUR models using the mean Settlers Park reference value as a temporal covariate. In sensitivity analyses, LUR models were re-fit using mean reference values from Settlers and Braddock reference sites. Source terms with the strongest univariate correlation with the temporally adjusted pollutant were then incorporated. Regression models were iteratively fit to assess overall model improvement at each stage, using the coefficient of determination (R^2), and removing non-significant covariates in order of descending p-value. Covariates were removed if variance inflation factor (VIF) was greater than 2. Interaction terms for inversion frequency, elevation, and wind speed were tested, and the final LUR models were determined, in which all retained covariates were significant ($p<0.05$).

Residuals from the final LUR models were mapped to identify systematic spatial variation, and the process identified locations poorly predicted by LUR, suggesting incorporation of additional covariates (i.e. inverse distance to NEI sites, binary elevation). Semivariograms of residuals were created in GIS, and residuals were mapped against latitude and longitude to explore residual patterns. Spatial autocorrelation between monitoring locations was tested using Moran's I. Generalized additive models (GAM) assessed spatial correlation across monitoring

sites. Predicted $PM_{2.5}$ concentrations and BC absorbance were made on a regular $100m^2$ grid, which was then further smoothed using inverse distance weighting (IDW), allowing spatial influence from nearest grid cell centroids. Isolines were calculated to connect points of equal concentration values and create contour lines showing the amount and rate of change across the IDW surfaces. Contour intervals of 2 $\mu g/m^3$ for and 0.5 abs units were chosen as the most visually representative for $PM_{2.5}$ and BC respectively.

Scatterplots were examined to assess the fit between each significant predictor and pollutant concentrations, to ensure that covariate selection was robust, and not reliant on outlier source values. Likewise, the fit of each additional term was tested against the residual of the prior model in the sequential model-building process. Model residuals were examined to ensure normality, and predicted pollutants were compared to observed concentrations, and model fit was examined by scatterplots. In all cases, selected covariates retained significance, and contributed to model fit. For LUR validation, 20% of sites (n=7 sites) were removed, the LUR model was re-fit and used to predict pollutant concentrations at the 7 withheld sites. Covariate selection was assessed by removal of outliers and influential points. Tree structures and Random Forest automated methods output were used for suggested ordering of covariates. Moran's I determined no spatial autocorrelation, and GAM models determined no spatial correlations across monitoring locations; hence no residual smoothing was performed. Sensitivity to model building was assessed using different temporal adjustment methods and modeling covariates against temporally adjusted pollutant concentrations to determine percentage of spatial variation across the eight LUR models.

For year 1 summer sampling, the final LUR model for $PM_{2.5}$ (R^2=0.77) includes the weekly temporal term, land use of commercial and industrial parcels within a 200m buffer, and

land use of industrial parcels within a 750m buffer (Table 6). For year 2 summer sampling, the final model for $PM_{2.5}$ (R^2=0.86) includes the weekly temporal term, SO_2 emissions within a 300m buffer, land use of commercial and industrial parcels within a 200m buffer, and wind direction (Table 7) (Figure 20).

For year 1 summer sampling, the final model for BC (R^2=0.64) includes the weekly temporal term, land use of industrial parcels within a 750m buffer, and elevation within a 1000m buffer (Table 6). For year 2 summer sampling, the final model for BC (R^2=0.72) includes the weekly temporal term, land use of commercial and industrial parcels within a 1000m buffer, SO_2 emissions within a 300m buffer, and wind direction (Table 7) (Figure 21).

For year 1 winter sampling, the final LUR model for $PM_{2.5}$ (R^2=0.71) includes the weekly temporal term, land use of commercial and industrial parcels within a 200m buffer, and average wind speed (m/s) (Table 6). For year 2 winter sampling, the final model for $PM_{2.5}$ (R^2=0.75) includes the weekly temporal term, SO_2 emissions within a 300m buffer, land use of commercial and industrial parcels within a 200m buffer, and number of signaled intersections within a 750m buffer (Table 7) (Figure 22).

For year 1 winter sampling, the final model for BC (R2=0.76) includes the weekly temporal term, land use of industrial parcels within a 750m buffer, signaled intersections within a 500m buffer, average wind speed (m/s), and elevation within a 1000m buffer (Table 6). For year 2 winter sampling, the final model for BC (R2=0.56) includes the weekly temporal term, land use of commercial and industrial parcels within a 1000m buffer, and SO_2 emissions within a 300m buffer (Table 7) (Figure 23).

Table 6. Year 1 inversion-focused LUR covariates and model fits for pollutants.

		LUR Model							
	Covariates	β	p-value	RMSE	IQR of source indicator	Conc. increase per source indicator	VIF	Adj R^2	Seq R^{2a}
Summer $PM_{2.5}$ ($\mu g/m^3$)[b]	Intercept	-0.58	0.71	--	--	--	--	--	--
	Weekly Reference PM	1.12	<0.0001	3.15	--	--	0.99	0.65	0.66
	Land Use (Com + Ind) at 200 meters	3.6x10^-6	0.05	2.83	391037	1.41	0.84	0.72	0.73
	Land Use (Industry) at 750 meters	8.6x10^-7	0.03	2.66	1482408	1.27	0.84	0.75	**0.77**
Summer BC (abs)[b]	Intercept	2.18	0.11	--	--	--	--	--	--
	Weekly Reference BC	2.53	0.0007	0.91	--	--	0.91	0.24	0.26
	Land Use (Industry) at 750 meters	2.8x10^-7	0.01	0.71	1482408	0.42	0.66	0.54	0.57
	Elevation at 1000 meters	-0.009	0.01	0.65	64.41	-0.60	0.62	0.61	**0.64**
Winter $PM_{2.5}$ ($\mu g/m^3$)	Intercept	10.58	0.004	--	--	--	--	--	--
	Weekly Reference PM	0.91	0.0004	2.40	--	--	0.69	0.45	0.47
	Land Use (Com + Ind) at 200 meters	4.7x10^-6	0.0002	2.12	391037	1.84	0.98	0.57	0.60
	Wind Speed (m/s)	-2.18	0.001	1.84	1.10	-2.40	0.69	0.68	**0.71**
Winter BC (abs)	Intercept	3.10	0.12	--	--	--	--	--	--
	Weekly Reference BC	0.60	0.82	0.54	--	--	0.54	0.02	0.04
	Land Use (Industry) at 750 meters	1.7x10^-7	0.0006	0.42	1482408	0.25	0.63	0.38	0.42
	Signaled intersections within 500 meters	0.05	0.01	0.36	3	0.14	0.74	0.56	0.60
	Wind Speed (m/s)	-0.30	0.001	0.31	1.10	-0.33	0.87	0.68	0.71
	Elevation at 1000 meters	-0.005	0.02	0.28	64.41	-0.32	0.37	0.72	**0.76**

[a]Seq R^2 is the sequential model fit for each additional term incorporated into model.
[b]One outlier removed for LUR modeling.

Table 7. Year 2 24-hour integrated LUR covariates and model fits for pollutants.

		LUR Model							
	Covariates	β	p-value	RMSE	IQR of source indicator	Conc. increase per source indicator	VIF	Adj R^2	Seq R^{2a}
Summer $PM_{2.5}$ ($\mu g/m^3$)	Intercept	-2.18	0.10	--	--	--	--	--	--
	Weekly Reference PM	1.20	<0.0001	1.89	--	--	0.97	0.65	0.65
	SO_2 emissions at 300 meters	1.2x10^-3	0.0002	1.63	370.62	0.44	0.88	0.71	0.75
	Land Use (Com + Ind) at 200 meters	2.0x10^-6	0.04	1.50	321526	0.64	0.94	0.77	0.79
	Wind Direction	--	--	1.26	1	--	0.94	0.84	**0.86**
	Blowing from NW/W	1.64	0.0005	--	--	1.64	--	--	--
	Blowing from SW/S	--	--	--	--	--	--	--	--
Summer BC (abs)	Intercept	-0.23	0.69	--	--	--	--	--	--
	Weekly Reference BC	1.28	0.03	0.59	--	--	0.93	0.10	0.12
	Land Use (Com + Ind) at 1000 meters	6.3x10^-8	0.0002	0.44	3957089	0.25	0.81	0.49	0.51
	SO_2 emissions at 300 meters	3.3x10^-4	0.0002	0.39	370.62	0.12	0.93	0.61	0.64
	Wind Direction	--	--	0.34	1	--	0.80	0.69	**0.72**
	Blowing from NW/W	0.39	0.004	--	--	0.39	--	--	--
	Blowing from SW/S	--	--	--	--	--	--	--	--
Winter $PM_{2.5}$ ($\mu g/m^3$)	Intercept	-1.06	0.47	--	--	--	--	--	--
	Weekly Reference PM	1.26	<0.0001	2.12	--	--	0.94	0.51	0.52
	SO_2 emissions at 300 meters	8.4x10^-4	0.03	2.00	370.62	0.31	0.89	0.56	0.58
	Land Use (Com + Ind) at 200 meters	3.1x10^-6	0.02	1.74	321526	1.00	0.80	0.67	0.70
	Signaled intersections within 750 meters	0.10	0.01	1.59	6	0.60	0.83	0.72	**0.75**
Winter BC (abs)	Intercept	-0.17	0.60	--	--	--	--	--	--
	Weekly Reference BC	1.26	<0.0001	0.65	--	--	0.97	0.26	0.28
	Land Use (Com + Ind) at 1000 meters	7.5x10^-8	0.001	0.55	3957089	0.30	0.94	0.47	0.50
	SO_2 emissions at 300 meters	2.4x10^-4	0.05	0.52	370.62	0.10	0.93	0.52	**0.56**

[a]Seq R^2 is the sequential model fit for each additional term incorporated into model.

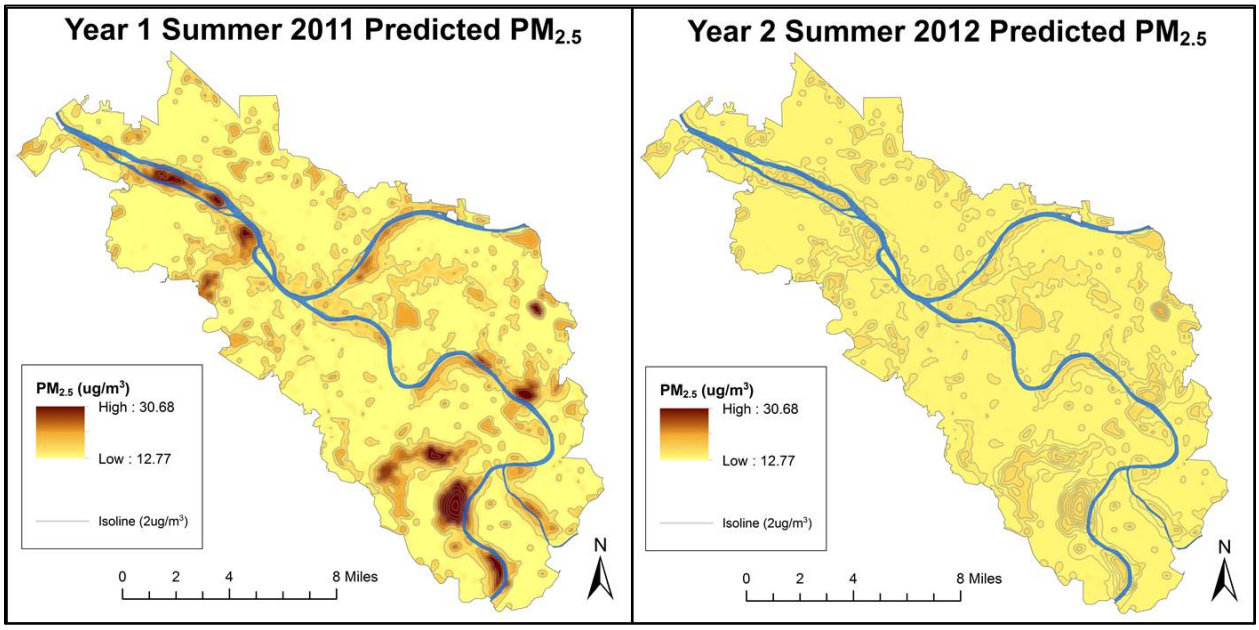


Figure 20. Predicted $PM_{2.5}$ exposure surface maps for summer year 1 (left) and year 2 (right) sampling.

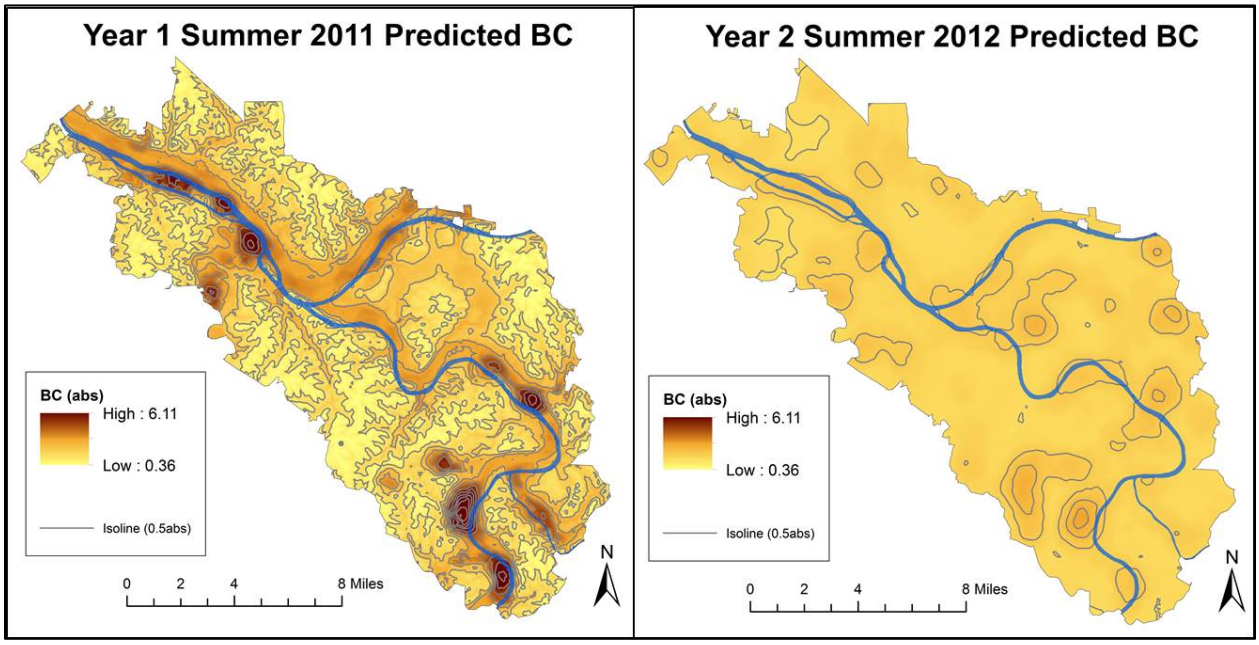


Figure 21. Predicted BC exposure surface maps for summer year 1 (left) and year 2 (right) sampling.

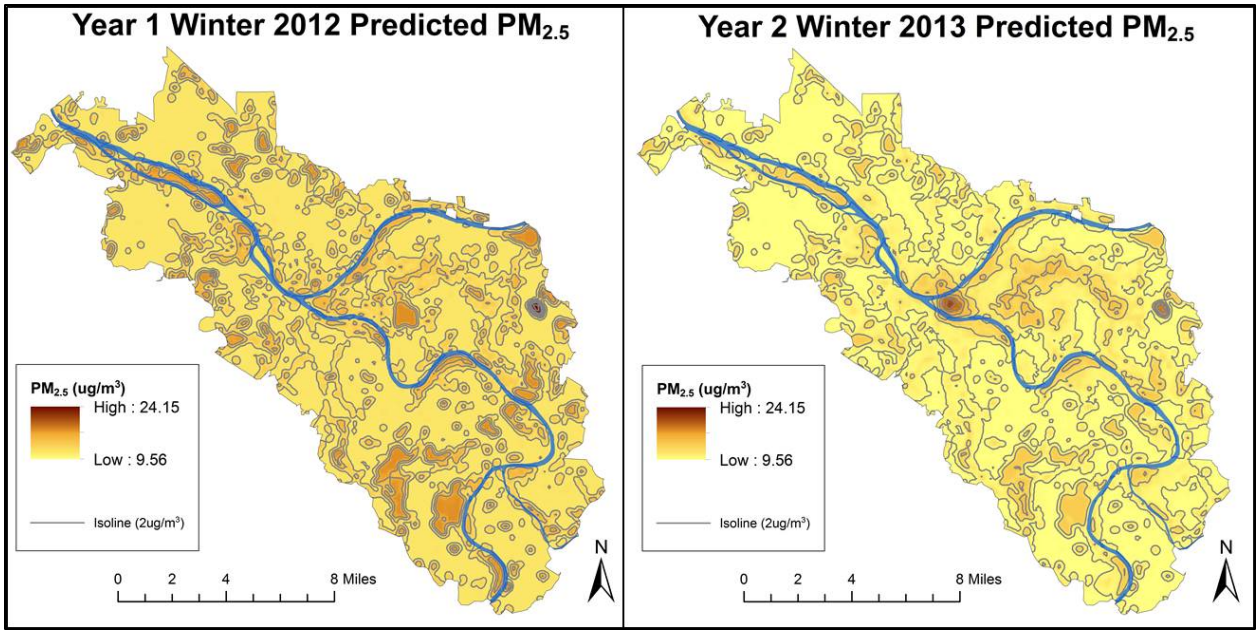


Figure 22. Predicted $PM_{2.5}$ exposure surface maps for winter year 1 (left) and year 2 (right) sampling.

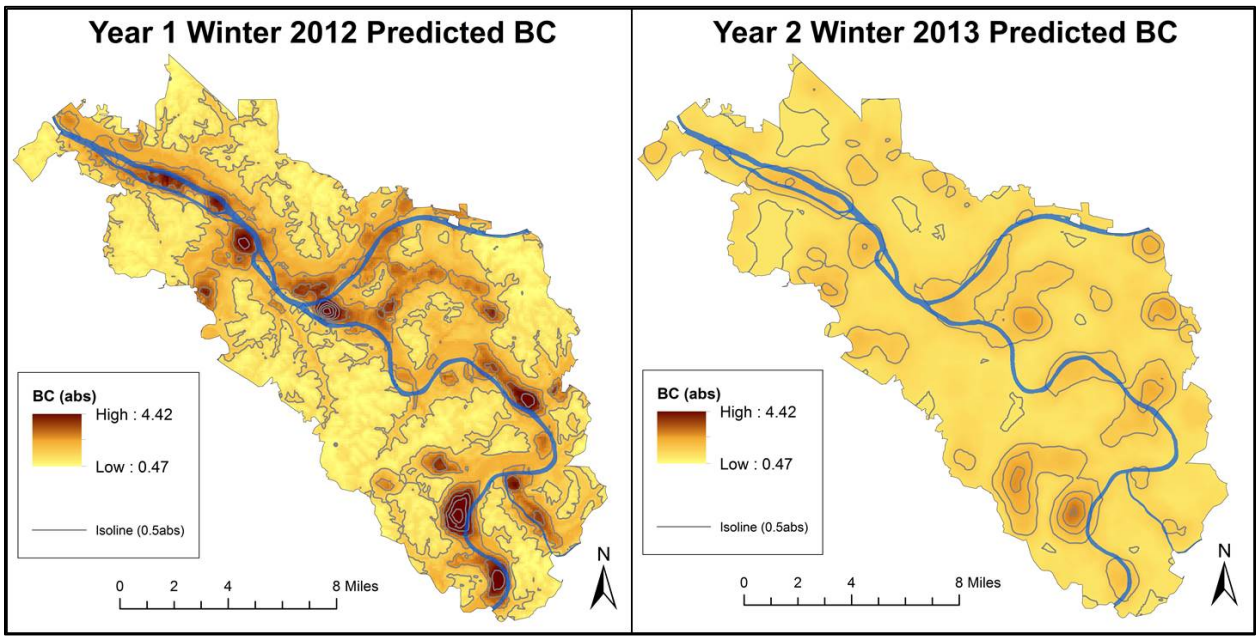


Figure 23. Predicted BC exposure surface maps for winter year 1 (left) and year 2 (right) sampling.

3.1.4 Why Sample Across the County?

Outdoor pollutant concentrations across 37 citywide distributed sites were determined for two years from summer 2011 to winter 2013. Pollutant temporal trends were observed between reference sites for both seasons and years, and spatial variability of pollutants across the sampling domain was found using GIS and our classification system to obtain a random stratified sample of monitoring locations. Seasonal, pollutant-specific LUR models predicted 56 to 86% of variability in pollutant concentrations, as land use, industrial emissions, wind speed and direction, and elevation covariates were significant. LUR models were similar within years of sampling, but differed between years according to sampling methodology. Elevated $PM_{2.5}$ and BC concentrations were found at sites near industry or in valleys compared to sites further from industry or not in valleys.

Year 1 summer and winter inversion-focused sampling explained 71-77% of $PM_{2.5}$ variability by temporal trends and land use of commercial and industrial parcels within a 200m buffer. Year 2 summer and winter 24-hour integrated sampling explained 75-86% of $PM_{2.5}$ variability by temporal trends, SO_2 emissions within 300m, and land use of commercial and industrial parcels within a 200m buffer. Inversion-focused and 24-hour integrated LUR $PM_{2.5}$ models are very comparable by season and are driven temporally by the background reference site and locally by land use.

When comparing inversion-focused to 24-hour integrated sampling LURs for the summer, a greater percentage of explained variability in $PM_{2.5}$ (86% vs. 77%) was determined for year 2 sampling, but heightened spatial contrasts were seen during year 1. Specifically, SO_2 industrial emissions within a 300m buffer, and wind direction were found for year 2, but not year 1; these emissions may have been captured during hours of sampling other than the 6-11AM

timeframe. For comparing yearly winter LURs, similar variability in $PM_{2.5}$ (75% vs. 71%) was explained for both years. Our study captured heightened spatial source contrasts during year 1 sampling, as the range of predicted $PM_{2.5}$ concentrations for exposure surface maps was greater in year 1 compared to year 2.

Year 1 summer and winter sampling explained 64-76% of BC variability by temporal trends, a land use covariate of industrial parcels within a 750m buffer, and elevation at 1000m. Year 2 summer and winter 24-hour integrated sampling explained 56-72% of BC variability by temporal trends, SO_2 emissions within 300m, and land use of commercial and industrial parcels within a 1000m buffer. Though a traffic covariate (number of signaled intersections within a 500m buffer) was significant for predicting winter BC in year 1, traffic density was not a significant predictor. Our study was unable to identify presence of inversions as a significant predictor, but elevation acted as a source on its own (it was not found to be a modifier, as no interactions were significant), potentially as an indicator of inversion presence and the trapping of BC during the sampling interval of 6-11AM. For BC, this may reflect influence of local sources instead of long-range transport, which, based on temporal findings, may impact $PM_{2.5}$. Inversion-focused and 24-hour integrated LUR BC models are very comparable by season and are less temporally driven by the background reference site (compared to $PM_{2.5}$ models) and are more locally influenced by land use and elevation.

In comparing the yearly summer models for BC, a greater percentage of explained variability (72% vs. 64%) was determined for year 2 sampling, as SO_2 emissions within a 300m buffer, and wind direction were important; higher BC was predicted when winds were blowing from the northwest or west. For winter BC, more variability was explained in year one (76% vs. 56%), as number of signaled intersections within 500m, wind speed, and elevation within

1000m were found in year 1 but not year 2. Most importantly, like $PM_{2.5}$, a greater range of variability in BC absorbance was observed during year 1 summer and winter compared to year 2.

Strong $PM_{2.5}$ temporal trends were found during both years of sampling, where year 1 accounted for 66% of the variability in the summer and 47% in winter, and year 2 accounted for 65% of the variability in the summer and 52% in winter. BC temporal trends were weaker, where year 1 accounted for 26% of the variability in the summer and 4% in winter, and year 2 accounted for 12% of the variability in the summer and 28% in winter.

When examining meteorology across all models, the frequency of inversions within a given sampling session was not significant for LUR modeling, and an interaction term between inversions and other covariates was not significant in this study. The presence of inversions was greater in winter sampling compared to summer seasons. Inversion frequency does act as a modifier for elevation, but did not remain in final pollutant inversion-focused LUR models [54]. Possible explanations for not finding an inversion metric for final models include: (1) inversions were so frequent that not enough variability occurred to see differences, (2) inversion characterization is regional (taken from Pittsburgh International Airport) and may be incompatible with fine-scale spatial interactions. We also were unable to find interactions between elevation and other covariates. Wind speed was found to be significant for year 1 $PM_{2.5}$ and BC winter modeling, and wind direction was found to be significant in year 2 BC summer modeling. Winds were predominantly from the west or northwest, though some sessions had southerly or northerly winds, especially during year 2 summer sampling. Meteorological factors such as higher temperature and relative humidity have been found to play a role in higher $PM_{2.5}$ concentrations in the eastern United States, and although temperature and relative humidity were

collected from each sampling unit, these factors were not found to be significant predictors in LUR modeling [100].

Lack of explanation of $PM_{2.5}$ spatial variability across our sites potentially indicates regional contribution and secondary formation; however, Pittsburgh is comprised of complex terrain, and GAM models determined no spatial correlation across the monitoring sites. Sensitivity tests were performed in LUR modeling in which the temporal term was the average pollutant concentration of Braddock and Settlers for any given week, as well as the concentration found at Settlers only. LUR models did not change regardless of which temporal term was used for modeling, and the models presented included the temporal term from Settlers, the regional background site.

Improvement in LUR methodology includes increased focus on development of models and sampling scheme that can be transferred to other areas [106]. Differences in R^2 from models across different cities may be related to the original variability in measured concentrations and the complexity of the city [106]. Pittsburgh is comprised of complex topography and industrial sources, and the yearly sampling methodologies allowed us to build and compare LUR models from the same area. The inversion-focused sampling approach provided heightened spatial source contrasts in $PM_{2.5}$ and BC, compared to 24-hour integrated sampling. These methods indicated that sampling timeframe is important for LUR creation; since these models are important for deriving exposure estimates for health outcomes, the methodology (i.e. sampling time frame) used for collection of pollutants is influential and can differ within the same study location.

In comparison to other cities who have created LUR models, the New York City Community Air Survey (NYCCAS) sampled approximately 150 sites within a domain of 300

square miles [38]. Our sampling domain was a smaller domain to site ratio, consisting of 150 square miles and containing 37 sites. In Los Angeles, LUR models have been created from 23 sampling sites over an area of 38,031 square miles, and in Vancouver, LUR models have been derived from 80 sampling sites over an area of 849.42 square miles [118, 119]. Due to the complexity of the Pittsburgh region, we believe 37 distributed sites were feasible for coverage.

A limitation of the study was due to equipment availability, as monitoring instruments could not be paired to obtain an inversion-focused and 24-hour integrated sample simultaneously; therefore, sampling was split into two years. To assess inversion frequency, wind speeds, and wind direction, data were obtained from the meteorological station at Pittsburgh International Airport and used to characterize sampling sites. Inversion presence was assessed as percentage of days in which an inversion was detected, and there is potential of missing events based on environmental soundings only released twice a day. A final limitation could arise because for any given week of sampling, a combination of "low" and "high" elevation sites were explored and were given the same inversion frequency metric; considering that Pittsburgh topography is so diverse, inversion variability across all sites may not have been fully captured. Effects were tested separately within low/high elevation sites, although there is a decrease in sample size.

The year 1 inversion-based study allowed us to further explore specific hours (6-11AM) of sampling in which high $PM_{2.5}$ levels were detected in a mobile monitoring campaign across Braddock [107]. A random stratified sample of monitoring locations were identified based on GIS methods and Geospatial Modeling Environment (GME); results show that industry and elevation are important, and this reassures the sampling approach to capture spatial variability in pollutant concentrations. The LUR models will be used to derive exposure estimates for future

health outcomes studies, and exposure surface maps were created for both sampling methodologies. Factor analysis of PM constituents will be determined by each season, indicating specific grouping of metals and sources of $PM_{2.5}$. Other data collected include NO_2, O_3, and SO_2, and this data will be analyzed, LUR models built, and exposure surfaces created.

3.2 SOURCE APPORTIONMENT AND FACTOR ANALYSIS OF TRACE METALS

Inductively-coupled plasma mass spectrometry (ICP-MS) analyses were conducted by the Wisconsin State Laboratory of Hygiene following documented protocols (ESS INO Method 400.4; EPA Method 1638) [54]. Table 8 lists the constituents included in analyses, along with hypothesized sources. We performed an updated literature search to find previous source apportionment studies for source-specific elemental tracers of combustion emissions and related sources to find previous source apportionment studies for similar geographic areas in the eastern United States, within the last three decades [50, 111].

Table 8. Nitrogen dioxide and suite of particle constituents along with hypothesized sources based on literature.

	Traffic				Local/Regional	Long Range Transport		
Constituents	Motor Vehicle	Brake/Tire	Soil/Road Dust	Diesel	Fuel/ Oil	Coal/ Secondary	Steel Making	Wood/Vegetative Burning
NO_2	3							
EC	3, 4, 5, 25			8, 13, 19, 20, 22, 25				20
Al	25		18, 19, 20, 22, 24, 26, 27	22, 25				
As			22			1, 3, 13, 16, 23		
Ba	4	6, 10, 13, 17	13	5				
Ca	4, 5, 8	2, 6	2, 3, 5, 20, 24, 26, 27	8, 13, 20				
Cd	11	9				1		
Cr	11	9, 13	13	22		1	21	
Cu	3, 11	2, 6, 9, 13, 17	13, 18, 22	20				
Fe	4, 5, 12	2, 6, 10, 13	2, 5, 13, 18, 20, 22, 24, 26, 27	13, 19			3, 12, 18, 19, 21	
K	5		2, 26, 27					3, 14, 19, 20, 26
La	5				12			
Mg		13	29	13				
Mn		13	13, 18, 22	19		1	3, 12, 18, 19, 21	
Mo		2, 9, 13					21	
Ni	11	9			3, 4, 12, 15, 20, 22, 27	1, 7, 12		
P	8			8				
Pb	11, 12		13, 18			1	19, 21	
S	4, 12		3	8		12, 22		
Sb		6, 9, 13, 17				1		
Se						1, 3, 12, 13, 16, 22, 23, 26		
Si			3, 5, 19, 20, 26	13				
Sn		9						
Sr		4, 6, 9						
V	4				3, 4, 12, 15, 20, 27	7		
Zn	5, 11, 12, 27	2, 9, 13, 17	13, 18	20			12, 19, 21	

Darker shading refers to greater frequency of references: 1 (Aneja et al., 2006); 2 (Apeagyei et al.,2011) 3 (Thurston, 2011); 4 (Lall and Thurston 2006); 5 (Zhao 2006); 6 (Sternbeck 2002); 7 (de Foy et al., 2011); 8 (Spencer 2006); 9 (Figi et al., 2010); 10 (Gietl et al., 2010); 11 (Gunawardana et al., 2012); 12 (Hammond 2008); 13 (Schauer (2006); 14 (Fine, 2001); 15 (Viana et al., 2008); 16 (Salvador, 2007); 17 (Iijima, 2008); 18 (Irvine, 2009); 19 (Rizzo and Scheff, 2007); 20 (Qin, 2006); 21 (Pekney, 2006); 22 (Ogulei (2006); 23 (Morneo et al., 2007); 24 (Lough, 2005); 25 (Lough & Schauer, 2007); 26 (Lee, 2008); 27 (Li, 2004).

We performed a factor analysis (FA) with varimax rotation (resulting in orthogonal components) using PROC FACTOR in SAS version 9.3(SAS Institute Inc., Cary, NC) and R. To determine the optimal number of factors, we considered formal criteria including the eigenvalue-one criterion, scree test, and the proportion of variance accounted for, retaining components that account for at least 5% of the total variance. Factor loadings were sensitivity tested using cutoffs of 0.50, 0.60, and 0.70.

Factor scores were determined for each monitoring location, and LUR models were implemented using manual forward step-wise linear regression, to assess factor scores for the four separate seasons. The full set of source indicator covariates were modeled separately for each factor score and each season, and LUR methods were described elsewhere [120]. Final

factor score LUR models were determined, in which all retained covariates were significant ($p<0.05$).

Across the 37 monitoring locations, 27 constituents (25 particle constituents from ICP-MS analysis, NO_2 from UV-VIS, and BC from reflectance) were included in factor analysis for each of the four seasons of interest. Concentrations from year 1 summer 2011 and winter 2012 inversion-based sampling are summarized in Tables 9 and 10, and concentrations from year 2 summer 2012 and winter 2013 24-hour integrated sampling are summarized in Tables 11 and 12.

Year 1 Summer 2011 Factor Analysis

For year 1 summer 2011, six factors were determined to explain 78% of variability found in trace metals (Figure 24). Factor one was a combination of *brake and tire wear* (calcium, chromium, molybdenum, antimony, and strontium) and soil/road dust resuspension (aluminum, calcium, chromium) [121-136]. Factor two includes *brake and tire wear*, as cadmium, copper, iron, manganese, and nickel were correlated, as well as a steel making component (iron, manganese) [121, 122, 124-128, 134, 135, 137, 138]. Factor three includes a *steel making* component (manganese, lead, zinc) and soil/road dust resuspension (potassium, lead, manganese, zinc) [121, 127-130, 132, 134, 135, 137, 138]. Factor four includes *coal*, as arsenic, selenium, and thallium were correlated [129, 132, 135, 137, 139-141]. Factor five indicates *diesel/motor vehicle* as phosphorous, sulfur and zinc were correlated [130, 133, 136, 137, 142-144]. Factor six includes *diesel/motor vehicle* as black carbon and nitrogen dioxide were correlated [127, 131-136, 143, 144].

Table 9. Summary of summer 2011 outdoor concentrations for the 37 distributed sites, with percent above analytic LOD (=3*Standard Deviation).

	N (obs)	Mean	Median	Std Dev	Min	Max	% > LOD
$PM_{2.5}$ ($\mu g/m^3$)	37	14.35	14.68	3.97	1.33	22.71	1.00
BC (abs)	37	1.64	1.59	0.91	0.017	4.64	1.00
NO_2 (ppb)	37	12.59	10.59	6.63	4.46	27.72	1.00
Constituents measured by ICP-MS (ng/m^3)							
Al	37	36.84	32.93	30.03	<0.001	142.24	0.81
As	37	1.76	1.75	0.95	<0.001	4.61	0.97
Ba	37	13.89	7.47	20.82	<0.001	90.49	0.49
Ca	37	148.55	84.49	270.76	<0.001	1664.29	0.78
Cd	37	0.25	0.23	0.21	<0.001	1.01	0.95
Ce	37	0.065	0.053	0.049	<0.001	0.24	0.92
Cr	37	3.45	2.12	3.54	<0.001	11.90	0.95
Cs	37	0.070	0.022	0.20	<0.001	1.22	1.00
Cu	37	11.07	9.43	9.94	0.016	43.73	0.95
Fe	37	186.00	128.49	158.27	0.51	620.95	0.97
K	37	66.87	57.27	68.99	<0.001	395.95	0.97
La	37	0.04	0.030	0.038	0.0018	0.21	0.92
Mg	37	23.57	12.45	30.19	1.99	147.68	0.76
Mn	37	7.33	5.42	7.00	0.024	26.68	0.97
Mo	37	2.38	1.53	2.45	<0.001	10.67	0.97
Ni	37	2.11	1.41	2.01	<0.001	8.44	0.95
P	37	5.42	4.48	3.83	0.17	16.75	0.84
Pb	37	6.67	5.78	6.14	0.0025	34.04	1.00
S	37	1013.00	880.82	703.55	<0.001	3704	0.97
Sb	37	1.37	1.13	1.04	0.0043	4.14	0.97
Se	37	4.22	2.87	4.95	<0.001	23.88	0.68
Sr	37	0.99	0.70	1.09	<0.001	5.80	0.81
Tl	37	0.096	0.042	0.17	0.0014	0.90	1.00
V	37	0.52	0.52	0.25	<0.001	1.15	0.97
Zn	37	64.16	36.37	103.26	<0.001	515.88	0.95

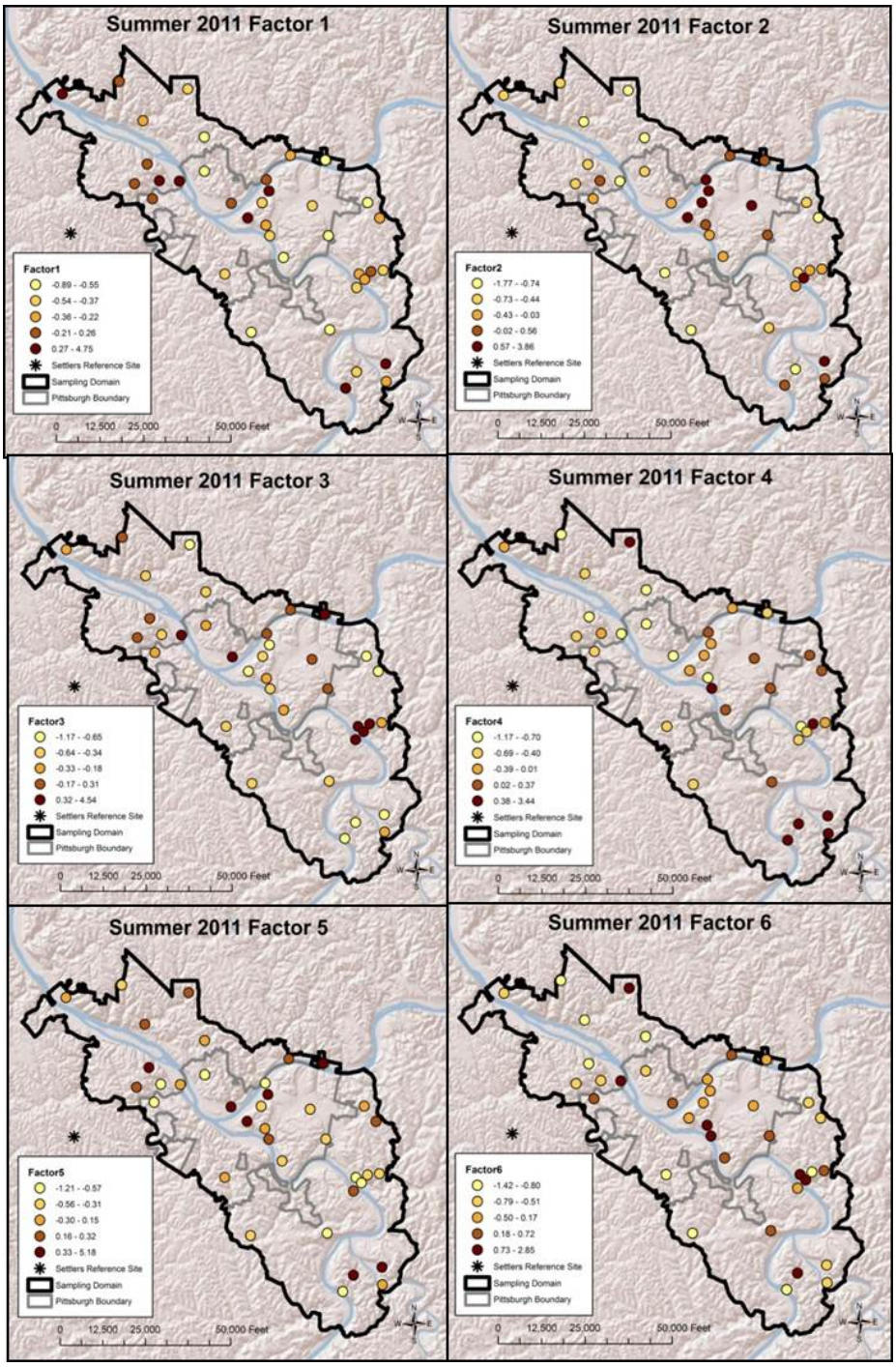
Winter 2012 Factor Analysis

For year 1 winter 2012, six factors were determined to explain 77% of variability found in trace metals, and the majority of sources were in the first factor. Factor one was a combination of *brake and tire wear* (calcium, cadmium, iron, magnesium, manganese, antimony, strontium, and zinc), *soil/road dust resuspension* (aluminum, arsenic, calcium, iron, potassium, manganese, lead, sulfur, zinc), *diesel* (aluminum, calcium, iron, magnesium, manganese, phosphorous, sulfur, zinc), and *steel making* (iron, manganese, lead, zinc) [121-138, 144, 145].

Factor two indicates *brake and tire wear*, as nitrogen dioxide, barium, chromium, and copper were correlated [122, 124-127]. Factor three consists of cerium, lanthanum, and molybdenum, but based on the current literature reviewed for this analysis, it is unclear what factor three indicates. Factor four indicates *fuel oil combustion* (nickel) [130, 132, 133, 135, 137, 143, 146]. Factor five indicates *coal* (selenium) [129, 132, 135, 137, 139-141]. Factor six indicates *diesel/vehicle* (black carbon) [127, 132-136, 143-145].

Table 10. Summary of winter 2012 outdoor concentrations for the 37 distributed sites, with percent above analytic LOD.

	N (obs)	Mean	Median	Std Dev	Min	Max	% > LOD
$PM_{2.5}$ ($\mu g/m^3$)	37	12.76	12.37	2.57	8.02	20.10	1.00
BC (abs)	37	1.34	1.24	0.53	0.70	2.72	1.00
NO_2 (ppb)	37	18.84	16.77	6.19	10.90	34.10	1.00
Constituents measured by ICP-MS (ng/m^3)							
Al	37	35.20	24.18	44.16	<0.0001	226.31	0.89
As	37	0.76	0.62	0.39	0.25	1.88	1.00
Ba	37	9.04	3.42	11.17	0.14	41.42	0.65
Ca	37	110.00	64.44	113.57	<0.0001	426.75	0.89
Cd	37	0.21	0.13	0.29	0.025	1.73	1.00
Ce	37	0.11	0.058	0.28	0.0021	1.72	1.00
Cr	37	1.69	1.41	1.70	0.0038	8.76	0.97
Cs	37	0.061	0.0079	0.13	<0.0001	0.63	1.00
Cu	37	4.24	3.50	2.83	0.28	13.15	1.00
Fe	37	158.71	87.49	202.91	10.01	1035.00	1.00
K	37	99.22	39.12	189.72	3.64	1120.00	1.00
La	37	0.058	0.017	0.17	<0.0001	0.99	0.95
Mg	37	10.48	8.13	9.03	0.48	38.29	0.97
Mn	37	6.94	3.11	9.77	0.57	53.37	1.00
Mo	37	3.58	2.04	4.57	0.15	20.65	1.00
Ni	37	1.15	0.65	1.35	0.047	6.02	0.97
P	37	5.60	3.76	5.98	<0.0001	27.25	1.00
Pb	37	4.36	3.15	3.64	0.42	16.30	0.97
S	37	554.95	487.54	259.56	120.11	1170.00	1.00
Sb	37	0.87	0.68	0.58	0.14	2.38	1.00
Se	37	0.63	1.13	3.98	<0.0001	11.380	0.97
Sr	37	0.56	0.30	0.60	<0.0001	2.17	1.00
Tl	37	0.043	0.026	0.052	0.0056	0.27	1.00
V	37	0.35	0.30	0.14	0.14	0.72	1.00
Zn	37	47.12	23.02	64.13	1.67	342.23	0.95


Summer 2011 Factor 1
Factor1
-0.89 - -0.55
-0.54 - -0.37
-0.36 - -0.22
-0.21 - 0.26
0.27 - 4.75
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 12,500 25,000 50,000 Feet
Summer 2011 Factor 2
Factor2
-1.77 - -0.74
-0.73 - -0.44
-0.43 - -0.03
-0.02 - 0.56
0.57 - 3.86
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 12,500 25,000 50,000 Feet
Summer 2011 Factor 3
Factor3
-1.17 - -0.65
-0.64 - -0.34
-0.33 - -0.18
-0.17 - 0.31
0.32 - 4.54
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 12,500 25,000 50,000 Feet
Summer 2011 Factor 4
Factor4
-1.17 - -0.70
-0.69 - -0.40
-0.39 - 0.01
0.02 - 0.37
0.38 - 3.44
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 12,500 25,000 50,000 Feet
Summer 2011 Factor 5
Factor5
-1.21 - -0.57
-0.56 - -0.31
-0.30 - 0.15
0.16 - 0.32
0.33 - 5.18
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 12,500 25,000 50,000 Feet
Summer 2011 Factor 6
Factor6
-1.42 - -0.80
-0.79 - -0.51
-0.50 - 0.17
0.18 - 0.72
0.73 - 2.85
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 12,500 25,000 50,000 Feet

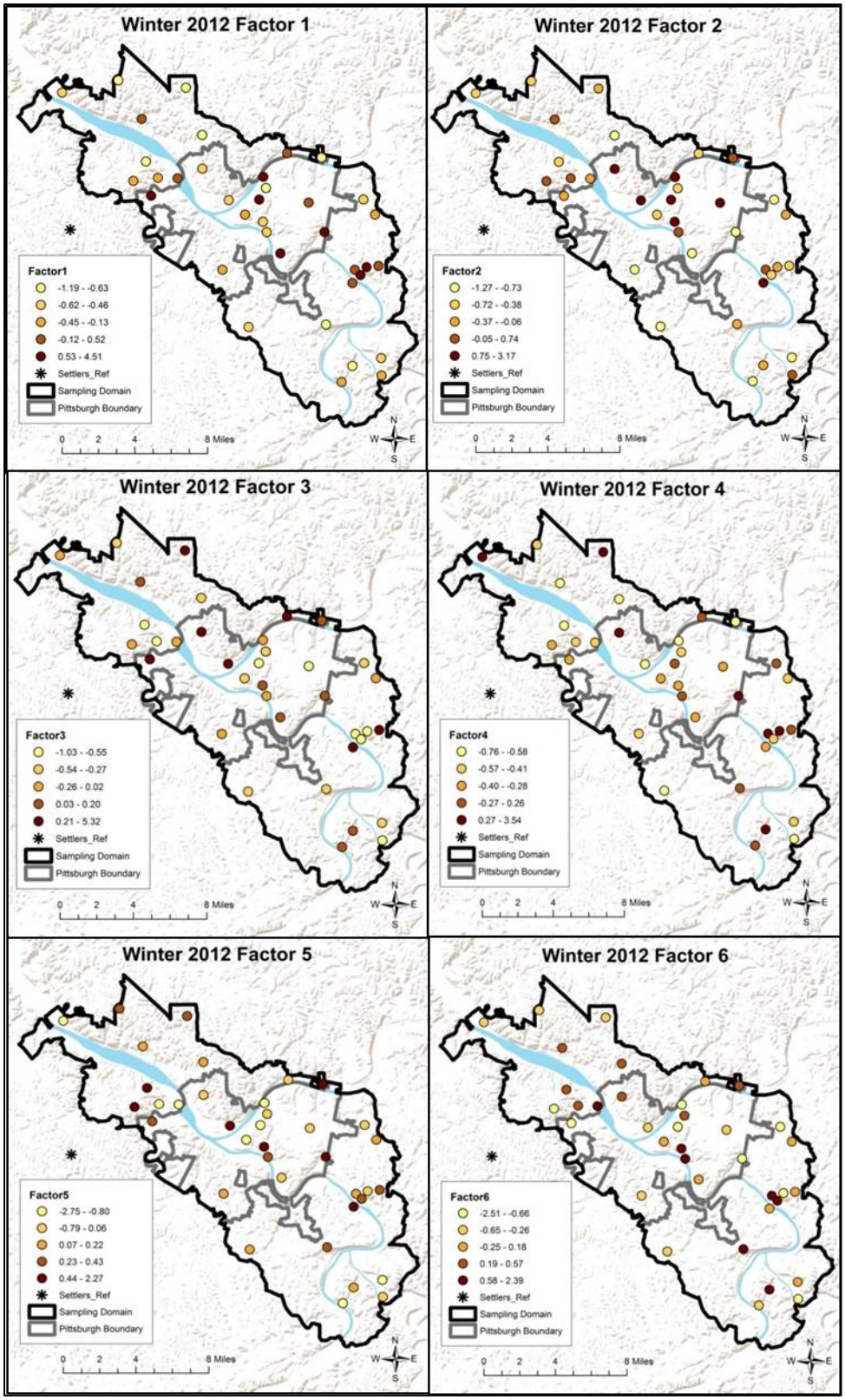


Figure 24. Factor scores mapped across summer 2011 and winter 2012 monitoring locations.

For trace metal analyses of inversion-based sampling, both year 1 summer 2011 and winter 2012 seasons included six factors. Summer factor one was a traffic combination of *brake/tire wear* and *soil/road dust*, with distance to bus depot as a significant LUR covariate. Winter factor one was also a traffic combination of *brake/tire wear* and *soil/road dust*. However, more sources were included in the first winter factor as *diesel* and *steel making* components were found. The clustering of many sources under one factor may be indicative of the presence of inversions during the Monday through Friday 6-11AM sampling, as pollutants from varying local sources, such as industrial and traffic emissions are trapped near ground level. Land use regression modeling of winter factor one indicated that the summed area of commercial and industrial parcels within a 300m buffer was significant, potentially capturing trapped traffic and industrial emissions.

For the other factors in year 1 inversion-focused sampling, summer 2011 factor two includes *brake/tire wear*, with the summed length of primary and secondary roadways within a 1000m buffer and inverse distance to railroad as significant covariates, and winter 2012 factor two indicates *brake/tire wear*, with signaled intersections within a 750m buffer as significant. Higher factor scores were seen at sites nearest to downtown Pittsburgh. Summer factor three includes a *steel making* component and *soil/road dust*, with summed industrial parcels within a 750m buffer as a significant covariate, and high factor scores at sites in Braddock, PA, whereas winter factor three was unclear when reviewing the literature; however, LUR suggested that mean density of heavy truck traffic within a 500m buffer and inverse distance to primary roadways were significant, indicating a *traffic* factor. Summer factor four includes *coal*, as summed density of total NEI pounds of $PM_{2.5}$, SO_2, NO_2, and VOCs emitted within a 750m

buffer was significant in LUR, and high factor scores were seen in the Clairton/Liberty area, whereas winter factor five includes *coal*. Summer factor five indicates *diesel/motor vehicle* as mean density of primary roadways within a 1000m buffer were significant in LUR, whereas winter factor four indicated *fuel/oil*, as SO_2 emissions within a 1000m buffer and distance to nearest primary roadways were significant. Summer factor six includes *diesel/vehicle* as inverse distance to NEI/TRI sites was significant, and winter factor six indicates *diesel/vehicle*, as signaled intersections within a 500m buffer and summed industrial parcels within a 750m buffer were significant.

Summer 2012 Factor Analysis

For year 2 summer 2012, six factors were determined to explain 78% of variability found in trace metals (Figure 25), and analysis was comparable to summer 2011. Factor one was a combination of *motor vehicle* (aluminum, barium, calcium, phosphorous, sulfur) and *brake and tire wear* (barium, calcium, magnesium). Factor two includes *steel making*, as iron, manganese, and zinc were correlated. Factor three includes *brake and tire wear* (copper, strontium) and *soil/road dust resuspension* (copper, potassium). Factor four includes *coal*, as arsenic, lead, and thallium were correlated. Factor five indicates *coal* (chromium). Factor six includes *coal/steel* (selenium).

Table 11. Summary of summer 2012 outdoor concentrations for the 37 distributed sites, with percent above analytic LOD.

	N (obs)	Mean	Median	Std Dev	Min	Max	% > LOD
$PM_{2.5}$ ($\mu g/m^3$)	37	13.94	13.34	2.01	11.26	22.59	1.00
BC (abs)	37	1.70	1.53	0.58	0.97	3.95	1.00
NO_2 (ppb)	37	10.37	10.24	4.53	3.35	21.31	1.00
Constituents measured by ICP-MS (ng/m^3)							

Table 11 continued

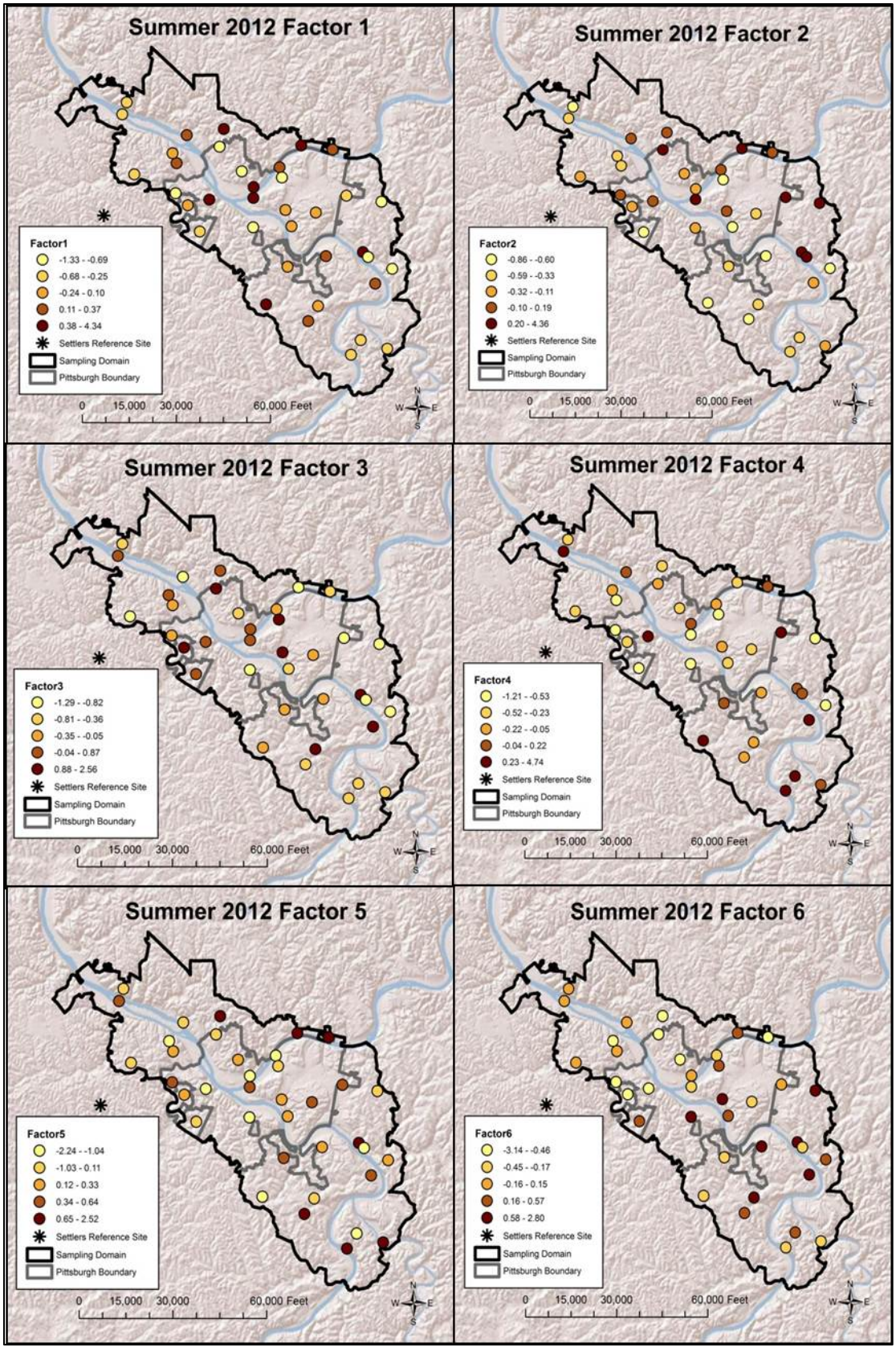
Al	37	34.34	29.92	24.22	<0.0001	139.02	0.97
As	37	1.28	1.00	0.78	0.28	4.95	1.00
Ba	37	4.14	3.30	2.61	0.12	10.41	0.84
Ca	37	156.42	128.13	151.56	8.70	742.48	0.97
Cd	37	0.14	0.13	0.077	0.0038	0.34	1.00
Ce	37	0.071	0.064	0.055	<0.0001	0.29	1.00
Cr	37	1.06	0.93	0.63	0.036	2.40	1.00
Cs	37	0.025	0.011	0.043	0.0011	0.18	1.00
Cu	37	5.71	3.71	6.10	0.071	30.32	0.97
Fe	37	110.83	90.66	86.26	3.41	515.56	1.00
K	37	93.05	81.69	55.98	3.77	244.51	0.97
La	37	0.037	0.030	0.029	0.0048	0.17	1.00
Mg	37	18.42	15.82	13.89	0.83	62.71	1.00
Mn	37	4.90	3.09	5.42	0.17	29.43	1.00
Mo	37	1.44	1.32	0.94	0.15	3.71	1.00
Ni	37	1.38	1.07	1.78	<0.0001	10.63	1.00
P	37	4.45	4.46	1.54	1.31	7.63	1.00
Pb	37	3.87	3.43	2.20	0.11	10.39	1.00
S	37	1032.00	1016.22	353.85	43.49	1679.00	1.00
Sb	37	1.05	0.96	0.43	0.050	1.85	1.00
Se	37	1.86	1.49	1.89	<0.0001	7.23	1.00
Sr	37	1.05	0.84	0.67	0.03	2.96	0.97
Tl	37	0.066	0.032	0.14	0.0065	0.87	1.00
V	37	0.49	0.45	0.15	0.28	0.89	1.00
Zn	37	23.79	21.44	14.97	5.22	75.40	1.00

Winter 2013 Factor Analysis

For year 2 winter 2013, four factors were determined to explain 88% of variability found in trace metals. Factor one was a combination of *motor vehicle* (aluminum, calcium, chromium, copper, nickel vanadium), *brake and tire wear* (calcium, chromium, copper, magnesium, nickel, strontium), *soil/road dust resuspension* (aluminum, calcium, chromium, copper, magnesium), *diesel* (aluminum, calcium, chromium, copper, magnesium), and *fuel oil combustion* (nickel, vanadium). Factor two indicates *motor vehicle/diesel* (black carbon, barium, copper, lanthanum, phosphorus, sulfur) and *brake and tire wear*, as barium, copper, antimony were correlated. Factor three indicates *coal* (cadmium, lead, selenium, thallium). Factor four indicates *steel making* (iron, manganese, lead, zinc).

Table 12. Summary of winter 2013 citywide concentrations for 37 distributed sites, with percent above analytic LOD.

	N (obs)	Mean	Median	Std Dev	Min	Max	% > LOD
$PM_{2.5}$ ($\mu g/m^3$)	37	11.26	11.12	2.01	8.01	18.92	1.00
BC (abs)	37	1.54	1.37	0.58	0.84	3.63	1.00
NO_2 (ppb)							
Constituents measured by ICP-MS (ng/m^3)							
Al	37	15.62	10.32	21.53	1.85	127.16	1.00
As	37	0.771	0.58	0.59	0.20	2.86	1.00
Ba	37	11.95	1.44	25.96	0.14	120.72	1.00
Ca	37	278.50	1009	772.58	<0.001	6089.97	1.00
Cd	37	0.41	0.17	0.95	0.012	4.77	1.00
Ce	37	0.24	0.032	0.95	0.010	5.76	1.00
Cr	37	1.08	0.43	2.27	<0.001	13.67	0.97
Cs	37	0.042	0.0093	0.095	0.0023	0.39	1.00
Cu	37	3.96	2.77	4.34	0.13	22.33	1.00
Fe	37	259.97	53.38	675.82	6.03	3661	1.00
K	37	55.79	40.70	46.44	10.24	219.93	1.00
La	37	0.031	0.021	0.043	0.0030	0.25	1.00
Mg	37	16.21	6.40	26.90	1.10	139.37	0.97
Mn	37	9.08	2.14	21.96	0.40	96.29	1.00
Mo	37	1.07	0.87	0.74	0.28	3.82	1.00
Ni	37	0.54	0.30	0.95	0.027	5.87	1.00
P	37	4.06	2.84	3.69	0.50	15.24	1.00
Pb	37	4.21	2.57	5.43	0.58	26.39	1.00
S	37	485.39	415.27	272.89	145.15	1313	1.00
Sb	37	0.65	0.53	0.51	0.080	2.48	1.00
Se	37	1.14	0.92	1.13	<0.001	5.82	0.86
Sr	37	0.43	0.23	0.55	0.011	3.02	1.00
Tl	37	0.078	0.016	0.17	0.0035	0.97	1.00
V	37	0.33	0.25	0.41	0.12	2.66	1.00
Zn	37	38.99	10.47	84.12	0.71	391.88	1.00


Summer 2012 Factor 1
Factor1
-1.33 - -0.69
-0.68 - -0.25
-0.24 - 0.10
0.11 - 0.37
0.38 - 4.34
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 15,000 30,000 60,000 Feet
N
W E
S
Summer 2012 Factor 2
Factor2
-0.86 - -0.60
-0.59 - -0.33
-0.32 - -0.11
-0.10 - 0.19
0.20 - 4.36
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 15,000 30,000 60,000 Feet
N
W E
S
Summer 2012 Factor 3
Factor3
-1.29 - -0.82
-0.81 - -0.36
-0.35 - -0.05
-0.04 - 0.87
0.88 - 2.56
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 15,000 30,000 60,000 Feet
N
W E
S
Summer 2012 Factor 4
Factor4
-1.21 - -0.53
-0.52 - -0.23
-0.22 - -0.05
-0.04 - 0.22
0.23 - 4.74
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 15,000 30,000 60,000 Feet
N
W E
S
Summer 2012 Factor 5
Factor5
-2.24 - -1.04
-1.03 - 0.11
0.12 - 0.33
0.34 - 0.64
0.65 - 2.52
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 15,000 30,000 60,000 Feet
N
W E
S
Summer 2012 Factor 6
Factor6
-3.14 - -0.46
-0.45 - -0.17
-0.16 - 0.15
0.16 - 0.57
0.58 - 2.80
Settlers Reference Site
Sampling Domain
Pittsburgh Boundary
0 15,000 30,000 60,000 Feet
N
W E
S

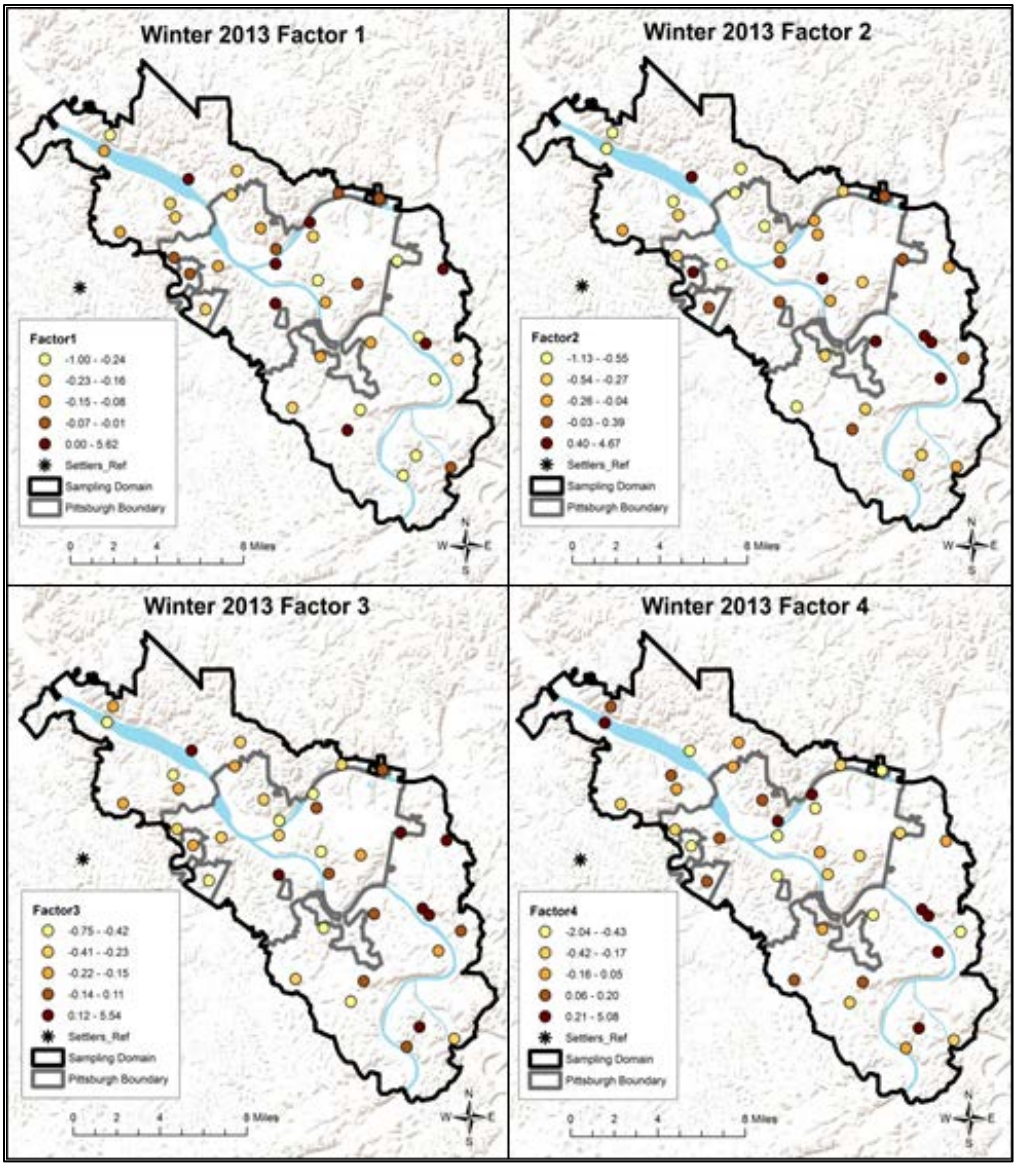


Figure 25. Factor scores across summer 2012 and winter 2013 monitoring locations.

For year 2 24-hour integrated sampling, summer 2012 factor one was a combination of *motor vehicle* and *brake and tire wear*, with mean density of buses within 750m significant, and winter 2013 factor one was a combination of *motor vehicle*, *brake and tire wear*, as well as *soil/road dust resuspension*, *diesel*, and *fuel oil combustion*; no spatial covariates were found for winter factor one LUR modeling. Again, a clustering of sources was found for year two winter

sampling, similar to year one winter. Winter factor two indicates *motor vehicle/diesel* and *brake and tire wear*, with signaled intersections within a 500m buffer and summed length of railroad within a 500m buffer as significant LUR covariates.

Summer 2012 factor two includes *steel making*, with SO_2 emissions within a 300m buffer, summed commercial and industrial parcels within a 1000m buffer, and signaled intersections within a 500m buffer significant, and higher factor scores were seen in Braddock, and winter factor four indicates *steel making*, with summed industrial parcels within a 500m buffer significant, and higher factor scores in Braddock. Summer factor three includes *brake and tire wear* and *soil/road dust resuspension*, which appears to be indicated in winter factor one; LUR modeling indicated that signaled intersections within a 500m buffer was significant. Summer factors four, five, and six include *coal*, with summed industrial emissions as significant covariates and higher factor scores in Clairton, whereas winter factor three indicates *coal*, with SO_2 emissions within a 300m buffer significant, and higher factor scores in Clairton as well.

The analyzed metal constituents used for source apportionment comprise a small fraction of total fine particulate matter, as organic chemicals, nitrates, dust particles, and allergens (i.e. pollen, mold spores) may also be present. Sulfur was the most predominant trace metal constituent detected using ICP-MS (54 to 70% of total mass on average). Sulfur air pollutants (impurities from coal and oil) from power plants include the primary pollutant sulfur dioxide (SO_2), as well as secondary pollutants, including sulfate particulate matter (SO_4) and sulfuric acid. SO_2 is a highly reactive gas, and the greatest sources of SO_2 emissions include fossil fuel combustion at power plants (73%) and other industrial facilities (20%) [147]. Additional sources include industrial extraction of metal from ore, and the burning of high sulfur-containing fuels by large ships and locomotives [147]. SO_2 can undergo chemical reactions in the air to form

sulfates (SO_4), which are found in secondary particulate matter. In the United States from 2001 to 2010, it has been found that annual total SO_2 emissions from power plants have decreased at a similar rate as sulfate concentrations, suggesting a linear relationship between the two [148].

In the year 2, 24-hour integrated citywide campaign, SO_2 emissions within a 300m buffer were found to be a significant predictor of $PM_{2.5}$ and BC variability across the sampling locations for both the summer and winter seasons. However, SO_2 emissions were not captured in the year 1 inversion-focused 6-11AM LUR models, indicating a greater level of emissions during different sampling hours. Within our citywide sampling domain, industrial facilities, such as the Edgar Thomson Steel Works, the Clairton Coke Works, and the Shenango Coke Works were included. Winds were predominantly blowing to the Pittsburgh region from the west/northwest, in which there are many industrial facilities and power plants located in Ohio, so long-range transport of particulate matter is a possibility [149, 150]. For $PM_{2.5}$, temporal terms explained 47 to 66% of the variability in concentrations in the models, indicating that a significant portion of $PM_{2.5}$ may be from long-range transport and secondary sulfate formation. Year 2 LUR models had higher temporal trends, as well as higher sulfur content for both the summer and winter sampling.

Because warmer temperatures favor chemical reactions involving SO_2, sulfates are produced more readily in the summer, and this was detected during both years of citywide sampling. Sulfur conversion ratios have been found to be higher in the summer compared to the winter, as well as increase with increasing ozone and relative humidity; this indicates that droplet and gas phase reactions are important for oxidation of SO_2 to sulfate [151]. For year 1, the mean percentage of summer and winter sulfur found across 37 distributed monitoring sites was 66% (SD = 14%) and 54% (SD = 12%) of the total trace metal constituent mass. For year 2, the mean

percentage of summer and winter sulfur was 70% (SD = 10%) and 64% (SD = 11%) of the total trace metal constituent mass. Because sulfur is such a predominant trace metal constituent, health effects related to sulfur dioxide and sulfates, such as cardiovascular disease, respiratory illness, and increased total mortality, should be further studied, especially in the Pittsburgh region [104] .

This two-year citywide study allowed us to further understand source apportionment using two sampling methodologies in an urban area with complex terrain, large industrial sources, and high traffic density areas. Year 1 sampling, which occurred at specific hours (Monday through Friday from 6-11AM) of sampling, was anticipated to capture heightened source signature contrasts because high $PM_{2.5}$ and PM_{10} levels were detected in a mobile monitoring campaign across Braddock [107]. Year 2 sampling occurred at a 24-hour 7-day integrated level in an attempt to capture pollutants across all hours of the day. Factor analysis of PM constituents was determined by each season, indicating specific grouping of metals and sources of $PM_{2.5}$, and further complementing our LUR models based off of this citywide study.

Table 13. Year 1 inversion-focused factor score LUR results.

Summer 2011 (Year 1: Inversion-Focused)		
Factor	**Proposed Source**	**Final LUR Modeling Covariates (R^2)**
1	Brake/Tire (Ca, Cr, Mo, Sb, Sr) Soil/Road Dust (Al, Ca, Cr)	Distance to bus depot (R^2=0.30)
2	Brake/Tire (Cd, Cu, Fe, Mn, Ni), Steel Making (Fe, Mn)	Summed length of primary and secondary roadways within a 1000m buffer Inverse distance to railroad (R^2=0.50)
3	Steel Making (Mn, Pb, Zn), Soil/Road Dust (K, Pb, Mn, Zn)	Summed area of industrial parcels within a 750m buffer (R^2=0.34)
4	Coal (As, Se, Tl)	Summed density of total NEI pounds of $PM_{2.5}$, SO_2, NO_2, and VOCs emitted within a 750m buffer Signaled intersections within a 500m buffer (R^2=0.34)

Table 13 continued

5	Diesel/Motor Vehicle (P, S, Zn)	Mean density traffic (primary roads) within a 1000m buffer (R^2=0.15)
6	Diesel/Motor Vehicle (BC, NO_2)	Inverse distance to NEI/TRI sites (R^2=0.21)
Winter 2012 (Year 1: Inversion-Focused)		
Factor	**Proposed Source**	**Final LUR Modeling Covariates (R^2)**
1	Brake/Tire (Ca, Cd, Fe, Mg, Mn, Sb, Sr, Zn), Soil/Road Dust (Al, As, Ca, Fe, K, Mn, Pb, S, Zn), Diesel (Al, Ca, Fe, Mg, Mn, P, S, Zn), Steel (Fe, Mn, Pb, Zn)	Summed area of commercial and industrial parcels within a 300m buffer (R^2=0.29)
2	Brake/Tire (NO_2, Ba, Cr, Cu)	Signaled intersections within a 750m buffer (R^2=0.20)
3	Unclear (Ce, La, Mo)	Mean density of heavy truck traffic within a 500m buffer Inverse distance to primary roadways (R^2=0.43)
4	Fuel Oil Combustion (Ni)	The summed density of pounds of SO_2 emitted within a 1000m buffer Distance to nearest primary roadway (R^2=0.47)
5	Coal (Se)	Average elevation within a 50m buffer (R^2=0.12)
6	Diesel/Motor Vehicle (BC)	Signaled intersections within a 500m buffer Summed area of industrial parcels within a 750m buffer (R^2=0.34)

Table 14. Year 2 24-hr integrated factor score LUR results.

Summer 2012 (Year 2: 24-hr Integrated)		
Factor	**Proposed Source**	**Final LUR Modeling Covariates (R^2)**
1	Diesel/Motor Vehicle (Al, Ba, Ca, P, S), Brake/Tire (Cu, Sr)	Mean density of bus traffic within a 750m buffer (R^2=0.28)
2	Steel Making (Fe, Mn, Zn)	Summed density of pounds of SO_2 emitted within a 300m buffer Summed area of commercial and industrial parcels within a 1000m buffer Signaled intersections within a 500m buffer (R^2=0.44)
3	Brake/Tire (Cu, Sr), Soil/Road Dust (K, Cu)	Signaled intersections within a 500m buffer (R^2=0.47)
4	Coal (As, Pb, Tl)	Summed density of total NEI pounds of $PM_{2.5}$, SO_2, NO_2, and VOCs emitted within a 750m buffer (R^2=0.60)

Table 14 continued

5	Coal (Cr)	Summed density of total NEI pounds of $PM_{2.5}$, SO_2, NO_2, and VOCs emitted within a 1000m buffer (R^2=0.14)
6	Coal/Steel (Se)	No spatial covariates
Winter 2013 (Year 2: 24-hr Integrated)		
Factor	**Proposed Source**	**Final LUR Modeling Covariates (R^2)**
1	Motor Vehicle (Al, Ca, Cr, Cu, Ni, V), Brake/Tire (Ca, Cr, Cu, Mg, Ni, Sr), Soil/Road Dust (Al, Ca, Cr, CU, Mg), Diesel (Al, Ca, Cr, Cu, Mg), Fuel/Oil (Ni, V)	No spatial covariates
2	Diesel/Motor Vehicle (BC, Ba, Cu, La, P, S), Brake/Tire (Ba, Cu, Sb)	Signaled intersections within a 500m buffer Summed length of railroad within a 500m buffer (R^2=0.36)
3	Coal (Cd, Pb, Se, Tl)	The summed density of pounds of SO_2 emitted within a 300m buffer (R^2=0.25)
4	Steel Making (Fe, Mn, Pb, Zn)	The summed area of industrial parcels within a 500m buffer (R^2=0.28)

4.0 CHAPTER THREE

4.1 MANUSCRIPT 3: INDOOR AIR SAMPLING FOR MULTIPLE POLLUTANTS IN INDUSTRIAL COMMUNITIES IN PITTSBURGH

Pollutant concentrations, especially fine particulate matter ($PM_{2.5}$), are typically higher indoors compared to outdoors [152-154], and residential indoor concentrations are better predictors of personal exposures than residential outdoor measures [50]. Indoor air monitoring better characterizes personal exposures as time spent indoors can be as high as 87% per day [155].

Though ambient air pollution concentrations have decreased over the past three decades in the United States, systemic diseases associated with ambient air have increased [68, 70]. In the lower-income communities which often surround industrial sites in western countries, indoor residential exposures may be highly elevated, and a key priority for public health.

The communities of Braddock and Clairton, Pennsylvania, located east of Pittsburgh along the Monongahela River, have active industrial emission sources, which are some of the largest stationary sources of fine particles in Allegheny County. The Edgar Thomson Steel Works annually produces 725.22 tons of primary $PM_{2.5}$, whereas the Clairton Coke Works produces 1048.78 tons of primary $PM_{2.5}$ [156, 157] . Southeast of downtown Pittsburgh, the Clairton Coke Works in Clairton and the Edgar Thomson Steel Works in Braddock are located in

areas with high rates of childhood asthma [107]. The entire Metropolitan Statistical Area (MSA), an eight county region in Western Pennsylvania, is out of attainment; therefore, both Braddock and Clairton are situated in federal $PM_{2.5}$ non-attainment areas [108, 158, 159].

Intra- and inter-community spatial variability in outdoor air pollution concentrations can vary by orders of magnitude; these differences could be attributed to industrial and traffic sources, as well as source-concentration modifiers such as elevation and meteorology [50, 154].

In contrast, indoor sources, such as cooking and smoking can result in pollutant concentration variability between homes [160]. Cooking, cleaning, and indoor work characterized by movement have significantly increased PM concentrations, and outdoor particles have been found to contribute significantly to indoor pollution [161].

Recent outdoor saturation studies (summer 2011 to winter 2013) in Pittsburgh and surrounding communities have been used to assess spatial and temporal variability of fine particulate matter ($PM_{2.5}$), nitrogen dioxide (NO_2), and black carbon (BC) across Allegheny County with an emphasis on industrial sources, traffic density, and topography [113, 120]. These campaigns were used for development of pollutant-specific land use regression (LUR) models across Pittsburgh, and outdoor LUR-derived pollutant estimates could be tested in indoor multivariate modeling to determine an outdoor contribution to indoor pollution concentrations. Previous mobile $PM_{2.5}$ and PM_{10} monitoring was used in Braddock to obtain real-time $PM_{2.5}$ and PM_{10} concentrations, showing higher concentrations in morning hours versus afternoon, as well as increased PM_{10} concentrations near the Edgar Thomson Steel Works [107].

A variety of factors including high air pollution levels, low socioeconomic status, and race have been associated with increased asthma prevalence and morbidity [79, 80, 83]. $PM_{2.5}$, NO_2, and BC have been associated with adverse respiratory illness, such as asthma and

morbidity [22, 50, 110]. Concentrations of these pollutants can be impacted by both indoor and outdoor sources, as traffic measures have been important predictors [162]. The study area represents a confluence of these factors and provides an opportunity to better understand local indoor air pollution exposure patterns in industrial communities. For seasonal differences in $PM_{2.5}$, other studies found lower PM concentrations during summer months compared to winter [163, 164], as well as moderate to high indoor/outdoor (I/O) pollutant ratios [153, 165].

The primary objective of this study was to investigate pollutants in Braddock and Clairton households during summer 2011 and winter 2012. This was followed by seasonal, pollutant-specific multivariate modeling, including the contribution of outdoor pollution indoors. It was hypothesized that outdoor pollutant concentrations would strongly correlate with indoor concentrations. Indoor air monitors enabled examination of the mean variation in pollutant concentrations across homes near the active industrial sources, (I/O) ratios of pollutants, and the mean differences between summer and winter sampling sessions. It was hypothesized that pollutant concentrations (1) would be higher indoors, (2) would vary temporally by season, and (3) would vary spatially by proximity to local industrial sources and indoor sources.

4.1.1 Sampling Design

Families with at least one child participating in an asthmatic cohort at the Pediatric Environmental Medicine Center (PEMC) at Children's Hospital, Pittsburgh, PA, were invited to participate in an indoor air sampling campaign in the summer 2011 and winter 2012 to further investigate asthma etiology. A total of twenty-one homes in the Braddock and Clairton communities near Pittsburgh were sampled for a week duration during both the summer and winter seasons (Figure 26). Citing criteria included placement of samplers in the main activity

room, away from windows and combustion or heat sources. The summer sampling session occurred from July 25th to September 13th, 2011, and winter sampling occurred from January 30th to March 5th, 2012.

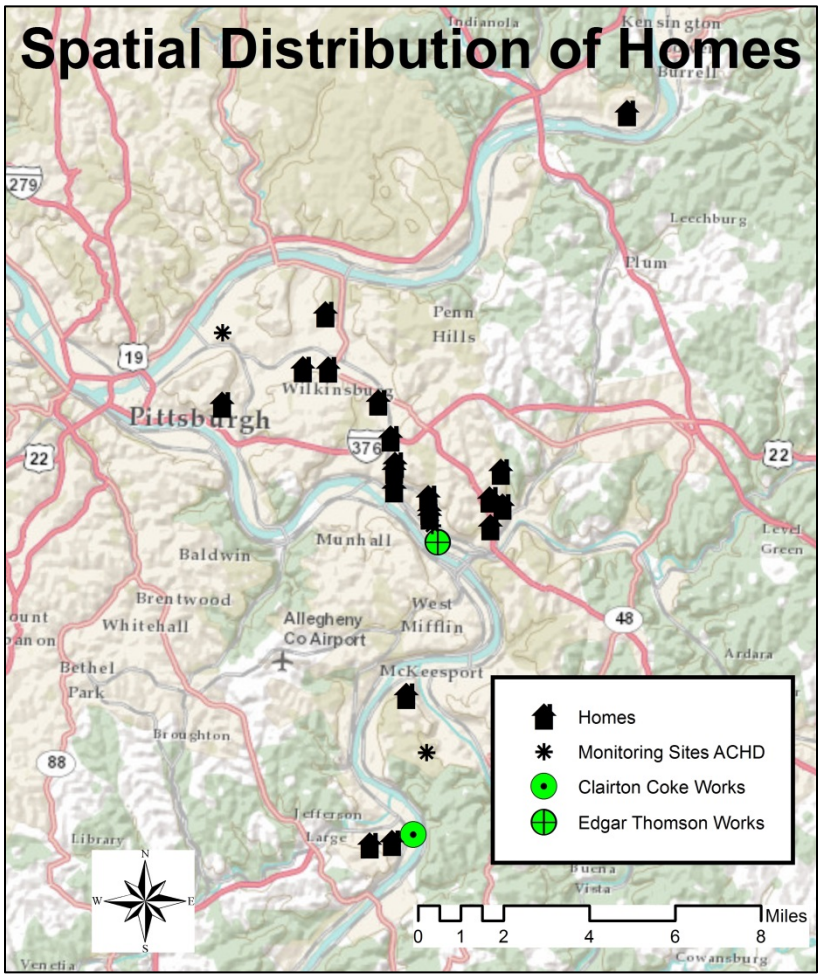


Figure 26. Spatial distribution of sampling homes, monitoring sites, and industrial sources.

Using a temperature and relative humidity controlled glove box (PlasLabs Model 890 THC), 37mm Teflon filters were pre-weighed (20.0°C and 35% RH) using an ultramicrobalance (Mettler Toledo Model XP2U) before deployment at the homes. After collection, the filters were post-weighed under the same conditions. A Harvard Personal Exposure Monitor (PEM) with a

MEDO linear-piston vacuum pump was used to collect $PM_{2.5}$. Passive diffusive Ogawa sampler badges were used to collect NO_2. A HOBO Data Logger (Onset devices) recorded temperature and relative humidity every five minutes. After three days of sampling, the PEM was replaced with a new one to avoid overload of particles. For both sessions, two homes were randomly selected for co-location of units. A standardized log sheet was used to record sampling start and stop times, and an indoor air pollution questionnaire was administered on the final day of sampling.

The $PM_{2.5}$ concentrations measured with the two PEMs for each home were averaged to determine an overall $PM_{2.5}$ concentration for the week-long sampling duration. Reflectometry was performed using an EEL43M Smokestain Reflectometer to determine black carbon absorbance units. Ogawa badges were stored in the refrigerator at 4°C and then analyzed using UV-VIS spectrophotometry to determine NO_2 concentrations (Thermo Scientific Evolution 60S UV-Visible Spectrophotometer). The badges were blank-corrected to determine NO_2 concentrations at the homes.

An adult over 18 in each home completed an indoor air pollution questionnaire for both summer and winter sampling sessions. Approximately 50 questions were administered, and included items on number of people/children in the home, smoking, cooking, ventilation, cleaning frequency, pesticide use, candle use, presence of pets, and other daily activities or characteristics of the home. Study data were collected and managed using REDCap (Research Electronic Data Capture) electronic data capture tools hosted at University of Pittsburgh [166]. Questionnaire covariates were created and correlations with $PM_{2.5}$, BC, and NO_2 were determined using SAS version 9.3 (SAS Institute Inc., Cary, NC).

To evaluate the influence of topography and relative distance to industries, spatial covariates were created to describe "elevation" and "distance to industry." Elevation above sea level was assessed at 100m buffers with the National Oceanographic and Atmospheric Digital Elevation Model. Addresses for the Clairton Coke Works and Edgar Thomson Steel Works were geocoded, and distance to industry was measured as Euclidean distance between each home and the centroid of the industrial facilities in Braddock and Clairton.

$PM_{2.5,}$ BC, and NO_2 exposure surface maps, derived from LUR models, for a domain of Allegheny County were used to predict outdoor $PM_{2.5}$ and NO_2 concentrations and BC absorbance at the monitoring locations. To determine outdoor pollution's contribution to the detected indoor concentrations, predicted outdoor pollutant concentrations were tested in multivariate linear regression modeling [120].

Outdoor concentration data from our prior citywide outdoor saturation study (summer 2011 and winter 2012) were obtained from an urban reference site in Braddock. Data in Braddock were obtained via gravimetric analyses of Teflon filters obtained from custom designed monitoring units with Harvard Impactors for a 6-11AM Monday through Friday sampling campaign. Using the outdoor Braddock monitoring data as reference, as well as concentrations predicted using our Pittsburgh LUR models from a previous study [120], specific indoor/outdoor ratios were then calculated for each home, to observe whether pollution levels were higher indoors or outdoors.

$PM_{2.5}$ and NO_2 hourly pollutant concentrations were obtained from Allegheny County Health Department for the Liberty and Lawrenceville monitoring locations (Figure 26). For these National Ambient Air Quality Standard (NAAQS) monitoring sites, $PM_{2.5}$ was determined via a gravimetric method by TEOM (Thermo Scientific TEOM 1400ab), and NO_2 was

determined by calculations from chemiluminescence of NOx and NO using Series A and E Nitrogen Oxides Analyzers (Teledyne-API Model 200). The hourly concentration data were then aggregated to coincide with indoor sampling hours.

4.1.2 Indoor Air Pollution Measurements

A mean indoor $PM_{2.5}$ concentration of 25.8 $\mu g/m^3$ (SD= 22.7 $\mu g/m^3$) was detected during summer, and 18.9 $\mu g/m^3$ (SD= 13.2 $\mu g/m^3$) during winter. A mean NO_2 concentration of 13.9ppb (SD= 7.2ppb) was detected during summer, and 26.7ppb (SD= 28.8ppb) during winter. For black carbon, a mean of 2.8 absorbance units (SD= 1.2abs) was found during summer, and 2.3 abs (SD= 1.4abs) during winter.

4.1.3 Differences in Seasonal Concentrations: Summer vs. Winter

For the summer sampling period, Pearson's correlation coefficients between pollutant concentrations and distance to nearest industry were -0.45 (p=0.04) for NO_2, -0.35 (p=0.13) for BC, and -0.22 (p=0.33) for $PM_{2.5}$. For the winter sampling period, no significant correlations between pollutant concentrations and distance to nearest industry were found (Table 15). Outdoor LUR predicted estimates of BC for summer were found to be significant in multivariate modeling (r=0.34) (Table 15) (Figure 27).

During summer, $PM_{2.5}$ concentrations correlated with temperature (r= 0.49) and number of cigarettes smoked (r=0.47). BC correlated with time spent cooking (r=0.41), number of cigarettes smoked (r=0.34), and number of children in the home (r=0.34). NO_2 concentrations

correlated with cleaning the kitchen (r=0.49), number of children in the home (r=0.38), and stovetop frying (r=0.30) (Table 15).

During winter indoor sampling period, $PM_{2.5}$ concentrations strongly correlated with number of children in the home (r=0.57), number of cigarettes smoked (r=0.54), and relative humidity (r=0.43). BC correlated with number of children in the home (r=0.56), supplemental heating (r=0.48), and stovetop frying (r=0.40). NO_2 concentrations correlated with number of cigarettes smoked (r=0.58) and number of children in the home (r=0.40) (Table 15).

Table 15. Meteorological, questionnaire-based indoor covariates, and outdoor-derived LUR covariates correlated with pollutants.

	Summer 2011			**Winter 2012**		
Covariate	**$PM_{2.5}$**	**BC**	**NO_2**	**$PM_{2.5}$**	**BC**	**NO_2**
Meteorological:						
Temperature (°F)	**0.49 (0.02)**	**0.32 (0.16)**	0.17 (0.45)	**-0.35 (0.11)**	-0.28 (0.21)	-0.29 (0.20)
Relative Humidity (% RH)	-0.17 (0.46)	0.15 (0.51)	-0.03 (0.89)	**0.43 (0.05)**	0.23 (0.32)	**0.38 (0.09)**
Reference Site $PM_{2.5}$	-0.14 (0.55)	-0.17 (0.45)	-0.30 (0.18)	-0.05 (0.83)	-0.18 (0.44)	0.15 (0.52)
Reference Site BC	-0.72 (<0.01)	-0.77 (<0.01)	-0.41 (0.07)	-0.28 (0.22)	-0.40 (0.07)	-0.10 (0.65)
Reference Site NO_2	-0.18 (0.44)	-0.19 (0.41)	-0.20 (0.38)	-0.05 (0.82)	-0.03 (0.90)	0.25 (0.28)
Questionnaire:						
# Cigarettes Smoked	**0.33 (0.14)**	**0.34 (0.13)**	0.11 (0.62)	**0.54 (0.011)**	**0.36 (0.11)**	**0.58 (0.01)**
# People in Home	0.12 (0.60)	0.25 (0.27)	0.27 (0.24)	**0.37 (0.10)**	**0.34 (0.13)**	0.18 (0.44)
# Children in Home	0.20 (0.38)	**0.34 (0.14)**	**0.38 (0.09)**	**0.57 (0.01)**	**0.56 (0.01)**	**0.40 (0.08)**
Windows Open	0.28 (0.22)	0.28 (0.22)	-0.16 (0.50)	**0.37 (0.10)**	0.19 (0.40)	0.29 (0.21)
Time Cooking	0.27 (0.24)	**0.41 (0.07)**	0.26 (0.26)	-0.04 (0.85)	0.15 (0.51)	-0.12 (0.62)
Stove Frying	0.27 (0.24)	0.29 (0.20)	**0.30 (0.18)**	**0.32 (0.15)**	**0.40 (0.073)**	0.08 (0.72)
Cleaning Kitchen	0.27 (0.23)	0.08 (0.72)	**0.49 (0.023)**	**0.36 (0.10)**	0.29 (0.20)	0.15 (0.52)
Spatial:						
Distance to Steel Mill	-0.22 (0.34)	**-0.35 (0.13)**	**-0.45 (0.04)**	-0.10 (0.66)	**-0.31 (0.17)**	-0.15 (0.51)
Elevation (100 meter buffer)	**-0.34 (0.13)**	**-0.32 (0.15)**	-0.23 (0.32)	**-0.38 (0.09)**	**-0.30 (0.18)**	**-0.50 (0.02)**

Table 15 continued

LUR Predicted $PM_{2.5}$	0.04 (0.86)	0.19 (0.43)	0.28 (0.22)	0.00 (0.99)	0.10 (0.65)	0.05 (0.83)
LUR Predicted BC	0.06 (0.79)	**0.34** **(0.14)**	**0.49** **(0.03)**	0.18 (0.44)	0.24 (0.30)	0.17 (0.45)
LUR Predicted NO_2	-0.06 (0.36)	-0.20 (0.38)	-0.14 (0.56)	-0.01 (0.96)	0.15 (0.52)	0.16 (0.49)

Correlations ≥ 0.30 are in bold ($p<0.20$).

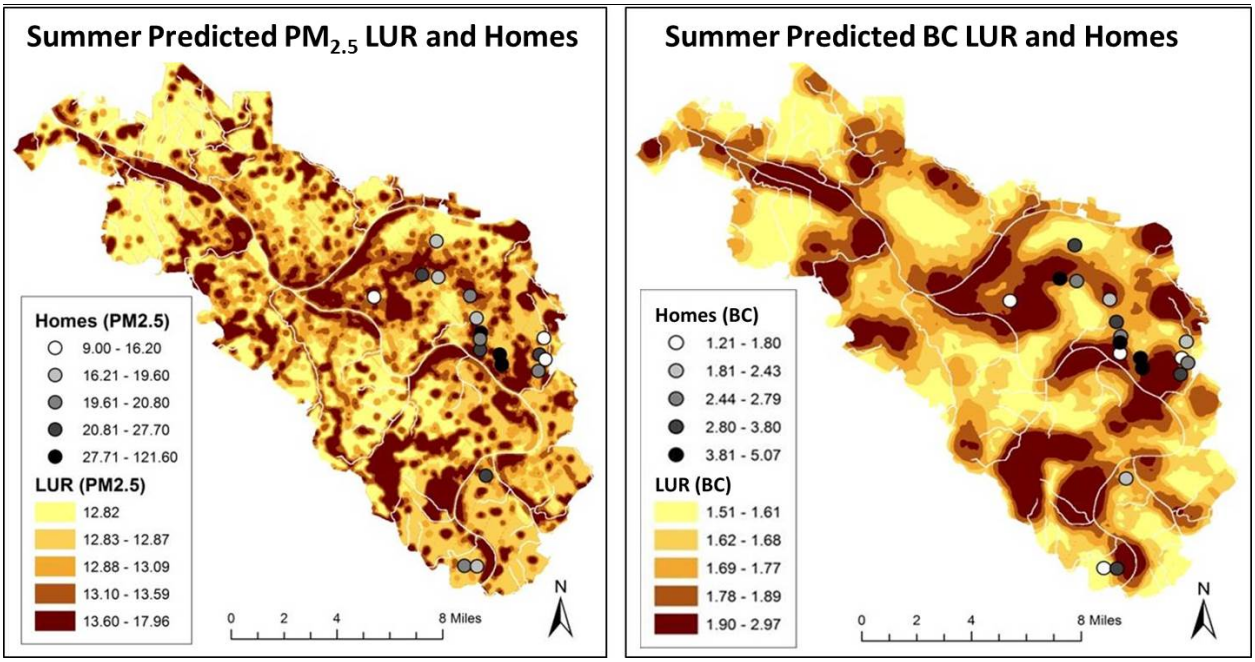


Figure 27. Summer $PM_{2.5}$ and BC indoor concentrations overlaid with LUR predicted estimates.

4.1.4 Comparing Indoor to Outdoor Pollutant Ratios

Higher concentrations were consistently found indoors compared to outdoors for $PM_{2.5}$ and BC. In the summer, I/O ratios for $PM_{2.5}$ averaged 1.97 (SD=1.78), for BC averaged 1.57 (SD=0.63), and for NO_2 averaged 0.94 (SD=0.51). In the winter, I/O ratios for $PM_{2.5}$ averaged 1.76 (SD=1.21), for BC averaged 1.74 (SD=0.99), and for NO2 averaged 1.04 (SD=1.01).

Using ambient data from Lawrenceville, PA, mean summer I/O ratios were 1.82 (SD=1.84) for $PM_{2.5}$ and 1.39 (SD=0.73) for NO_2 across sampling homes. For the winter, these

mean ratios were 1.53 (SD= 1.15) for $PM_{2.5}$ and 2.14 (SD= 2.50) for NO_2. Using ambient data from Liberty, a mean summer ratio was 1.59 (SD= 1.49) for $PM_{2.5}$. In the winter, a mean ratio was 2.05 (SD= 1.60) for $PM_{2.5}$.

Correlations between indoor and outdoor concentrations were fairly low, as $PM_{2.5}$ correlations were less than 0.10, BC were 0.24 to 0.34, and NO_2 were less than 0.20 across both seasons.

4.1.5 Seasonal, Pollutant-Specific Multivariate Models

Descriptive statistics, scatterplots, and histograms were used to characterize distributions of $PM_{2.5}$, BC, and NO_2 concentrations, spatial covariates (predicted LUR estimates, elevation, distance to mill) and temporal covariates (temperature, relative humidity) (Table 16). Categorical variables included the number of cigarettes smoked, frequency of cleaning the kitchen, and frequency of opening the windows. Before empirical model development, bivariate analyses were performed for pollutants and other variables. Data analysis and model-building were performed separately for $PM_{2.5}$ NO_2, and BC, and for each of the summer and winter seasons.

Multivariate linear regression models were built sequentially, using a manual forward-stepwise model building procedure. Covariates significant at $p < 0.20$ in bivariate analysis were individually incorporated into the model. Because of hypothesized importance of outdoor concentrations in the sampling area, LUR outdoor-derived pollutant-specific estimates were first incorporated into the model, followed by proximity to industry. After testing outdoor concentrations and predictors, indoor sources were ordered by strength of the bivariate correlation [162]. Model fit was assessed at each stage, using the coefficient of determination

(R^2), room mean square error (RMSE), variance inflation factor (VIF), p-value, and parameter estimate (β). At each stage, non-significant covariates were individually removed in order of descending p-value, and the model re-fit. Covariates were retained in final models if $p<0.10$. Statistical analyses were conducted using Proc Reg and Proc GLM in SAS version 9.3 (SAS Institute Inc., Cary, NC).

Scatterplots were examined to assess the fit between each significant predictor and pollutant concentrations, to ensure that covariate selection was robust, and not reliant on outlier source values. Likewise, the fit of each additional term was tested against the residual of the prior model in the sequential model-building process. Model residuals were examined to ensure normality, and predicted pollutants were compared to observed concentrations and model fit was examined through scatter plots. In all cases, selected covariates retained significance at $p<.10$, and contributed to model fit, improving R^2 by 0.01.

Table 16. Descriptive statistics for indoor air sampling pollutants and significant covariates.

	Summer 2011	**Winter 2012**
Mean $PM_{2.5}$ (μg/m^3)	25.8 (±22.7)	18.9 (±13.2)
Mean NO_2 (ppb)	13.9 (±7.2)	26.7 (±28.8)
Mean BC (abs)	2.8 (±1.2)	2.3 (±1.4)
Temperature (Mean, Min, Max °F)	77.4 (68-83)	68.7 (63-80)
Relative Humidity (Mean, Min, Max %)	55.62 (42-65)	33.1 (17-48)

Pearson correlations were determined between covariates and pollutant concentrations. For the summer, the final multivariate model for $PM_{2.5}$ (R^2=0.50) included number of cigarettes smoked in the home and temperature. The final model for BC (R^2=0.66) included frequency of open windows, number of cigarettes smoked, and predicted outdoor BC from a Pittsburgh LUR.

The final model for NO_2 (R^2=0.37) only included the frequency of cleaning the kitchen (Table 17).

For the winter, the final multivariate model for $PM_{2.5}$ (R^2=0.72) included relative humidity, number of cigarettes smoked, and frequency of open windows. The final model for BC (R^2=0.41) included number of children in the home. The final model for NO_2 (R^2=0.18) included elevation (Table 18).

Table 17. Summer 2011 multivariate model covariates and model fits for pollutants.

		Multivariate Model						
	Covariates	β	p-value	RMSE	VIF	IQR of source indicator	Conc. increase per source indicator	Seq R^{2a}
Summer $PM_{2.5}$ ($\mu g/m^3$)[b]	Intercept	-44.54	0.18	--	--	--	--	--
	Cigarettes Smoked	--	--	6.55	0.98	1	--	0.33
	1-4 cigarettes	11.58	0.006	--	--	--	11.58	--
	No cigarettes	0	--	--	--	--	--	--
	Temperature	0.98	0.03	5.83	0.99	3.92	3.84	**0.50**
Summer BC (abs)	Intercept	-2.54	0.41	--	--	--	--	--
	Summer 2012 Outdoor LUR Predicted BC (abs)	3.07	0.02	1.11	0.91	0.19	0.58	0.14
	Cigarettes Smoked	--	--	1.02	0.72	1	--	0.35
	>4 cigarettes	2.97	0.005	--	--	--	2.97	--
	1-4 cigarettes	2.09	0.05	--	--	--	2.09	--
	No cigarettes	0	--	--	--	--	--	--
	Windows Open	--	--	0.81	0.58	2	--	**0.66**
	> 12 hours	1.35	0.02	--	--	--	2.70	--
	5-12 hours	1.08	0.05	--	--	--	2.16	--
	1-4 hours	1.54	0.007	--	--	--	3.08	--
	< 1 hour	0	--	--	--	--	--	--
	Intercept	17.52	<0.0001	--	--	--	--	--

Table 17 continued

Summer NO_2 (ppb)	Frequency of cleaning the kitchen	--	--	6.03	--	2	--	**0.37**
	> 4 days per week	9.69	0.03	--	--	--	19.38	--
	4 days per week	8.66	0.02	--	--	--	17.32	--
	3 days per week	5.09	0.22	--	--	--	10.18	--
	< 3 days per week	0	--	--	--	--	--	--

[a]Seq R^2 is the sequential model fit for each additional term incorporated into model.
[b]One outlier was removed for PM modeling.

Table 18. Winter 2012 multivariate model covariates and model fits for pollutants.

		Multivariate Model						
	Covariates	β	p-value	RMSE	VIF	IQR of source indicator	Conc. increase per source indicator	Seq R^{2a}
Winter $PM_{2.5}$ ($\mu g/m^3$)	Intercept	16.92	0.07	--	--	--	--	--
	Relative Humidity (%)	0.88	0.001	12.17	0.96	11.74	10.33	0.19
	Cigarettes Smoked	--	--	9.28	0.35	1	--	0.58
	>4 cigarettes	22.33	0.002	--	--	--	22.33	--
	1-4 cigarettes	0.20	0.98	--	--	--	0.20	--
	No cigarettes	0	--	--	--	--	--	--
	Windows Open	--	--	7.77	0.96	1	--	**0.72**
	1-4 hours	11.05	0.01	--	--	--	11.05	--
	< 1 hour	0	--	--	--	--	--	--
Winter BC (abs)	Intercept	4.93	0.0009	--	--	--	--	--
	Number of children	--	--	1.20	--	2	--	**0.41**
	>4 children	3.54	0.02	--	--	--	7.08	--
	4 children	3.18	0.03	--	--	--	6.36	--
	3 children	2.78	0.08	--	--	--	5.56	--
	2 children	2.66	0.09	--	--	--	5.32	--
	< 2 children	0	--	--	--	--	--	--
	Intercept	79.07	0.02	--	--	--	--	--

Table 18 continued

Winter NO_2 (ppb)[b]	Elevation (meters)	-0.20	0.07	12.71	--	2	-0.40	**0.18**

[a]Seq R^2 is the sequential model fit for each additional term incorporated into model.
[b]One outlier removed for winter NO_2 modeling.

4.1.6 Why Perform Indoor Air Sampling?

Indoor pollutant concentrations, determined during summer 2011 and winter 2012, highlight the importance of air pollution exposures across and within homes near active steel mills, as well as the influence of indoor sources. Higher pollutant concentrations were observed indoors compared to outdoors, as I/O ratios were consistently greater than 1.0. Higher indoor $PM_{2.5}$ concentrations were found during the summer, whereas higher NO_2 concentrations were found during the winter.

It was hypothesized that outdoor concentrations would be strong predictors for indoor air pollution across homes near industrial facilities, but for the $PM_{2.5}$ models, smoking was the strongest predictor, along with meteorological terms such as temperature and relative humidity. In the winter, windows opened for greater than 1 hour per day, resulted in higher $PM_{2.5}$ concentrations, even in the smoking homes. Smoking is an important source of fine and coarse particulate matter indoors, and this was the most common covariate during modeling of pollutants within the sampled homes [155]. Another study by Wallace had found estimated increases in homes with smokers ranging from 25 to 45 $\mu g/m^3$ of $PM_{2.5}$ [155]. One home was removed from the statistical analysis because $PM_{2.5}$ was greater than 121 $\mu g/m^3$, and it was reported that more than 15 cigarettes were smoked per day indoors. Meteorological factors such as higher temperature and relative humidity have been found to play a role in higher outdoor

$PM_{2.5}$ concentrations in the eastern United States, and these predictors were important indoors [100]. For the summer $PM_{2.5}$ model, for every unit increase in temperature (°F), $PM_{2.5}$ concentrations increased by 0.98 $\mu g/m^3$. Time spent cooking was not found to be significant in predicting summer or winter PM concentrations.

For the summer, 66% of variability in BC was explained by frequency of open windows, number of cigarettes smoked, and outdoor predicted BC from our Pittsburgh-based LUR study. Our outdoor-derived summer BC absorbance value was a strong predictor for summer BC indoors. When we created this LUR model, land use of industrial parcels within 750m and elevation with 1000m were significant predictors of BC variability. For the winter, 41% of variability in BC was explained by number of children in the home, and this may indicate resuspension activity; we were unable to find a significant outdoor predictor. Smoking and frying food have both been found to emit particulates, which may include black carbon; however, cooking predictors were not significant in our modeling [155]. The frequency of open windows could be attributed to traffic, and our outdoor-derived LUR model did not include a traffic predictor. When windows were opened for greater than 12 hours per day (n=4), mean BC absorbance was 3.15 (SD=0.76abs), compared to windows open for less than 1 hour per day (n=8), in which mean BC was 2.24 (SD=1.22 abs). A study in Boston had found that indoor BC was associated with local traffic [162]. For summer BC and winter $PM_{2.5}$ models where windows were significant predictors, pollutant concentrations were higher when windows were open for longer periods of time. This may be indicative of infiltration from outdoor pollutant sources, such as traffic.

In the summer, only 37% of nitrogen dioxide variability was explained by frequency of cleaning the kitchen; cooking time did not result as a significant predictor, but frequency of

cleaning a kitchen could be a proxy for cooking activities. For the winter, less variability in NO_2 (18%) was explained, as elevation alone was an important predictor. As elevation increases, nitrogen dioxide levels have been found to decrease outdoors; outdoor predicted NO_2 estimates from LUR surfaces were not retained in the final model [113, 120]. In Boston homes, traffic sources were associated with NO_2, but we only found elevation to be a significant spatial variable [162].

Using residence-specific indicators and outdoor concentrations at ACHD sites, the majority of mean pollutant I/O ratios were greater than 1.0 (summer NO_2 = 0.94), indicating higher concentrations inside the home as compared to outside. Other studies found low and high correlations between indoor and outdoor pollutant concentrations when sampling inside and directly outside of homes; our study found low correlations between indoor and standard central monitoring stations [109, 154, 167]. Using residence-specific estimates determined from our Pittsburgh LUR models, the correlations between indoor and outdoor pollutant concentrations were also very low ($r < 0.30$). A study in Riverside, California found that outdoor concentrations near the homes were highly correlated with outdoor concentrations from a central site location. The same study also found very weak correlations between indoor and outdoor concentrations [168].

This study showed that daily activity patterns are important to adequately characterize exposure of individuals within the home. A strength of the indoor air sampling study is that it allowed us to quickly determine indoor weekly pollutant concentrations across homes near active industrial sites using a simple air sampling device; little maintenance of the units was required (the PEM only needed to be changed to avoid filter overload). 100% retention of sampling homes was achieved, so direct seasonal comparisons could be made. The questionnaire allowed

for quick assessment across a multitude of covariates to be used in multivariate linear regression modeling. One limitation was the sample size of only 21 homes; 56% of participants in the PEMC asthmatic cohort elected to partake in the indoor air sampling. Data primarily allowed us to gain an understanding of the complexity of exposure associated with indoor air pollution, and to determine the outdoor contribution to indoor air pollution through the use of our outdoor-derived exposure surface maps across Pittsburgh.

This sampling approach used in this study provided an exposure opportunity to evaluate for pollutants that are known to play a role in respiratory health. Further measuring of indoor pollutant levels is an important public health need, as lower income communities are often surrounded by industrial sites, potentially resulting in highly elevated residential exposures. Because the indoor pollutant concentrations were greater than outdoors, we should consider establishing health protective indoor air guidelines. This study evaluated indoor air in communities with active industrial emissions, and examined the outdoor contributions to indoor air pollution. It was hypothesized that outdoor pollution would be a strong predictor of indoor pollution, but only summer outdoor black carbon was a contributor in the models. The concentrations detected in the homes were discussed with the families after informed consent, along with potential sources of the pollution. This study is informative to parents about pollutant exposures, with potential to change daily activities such as smoking within the home, especially since it was a very strong predictor in $PM_{2.5}$ and BC models.

4.2 SOURCE APPORTIONMENT AND FACTOR ANALYSIS OF TRACE METALS BY SEASON

Fine particulate matter ($PM_{2.5}$) consists of a complex mixture of acids (nitrates, sulfates), organic chemicals, metals, and soil/dust particles. Specific source classes of $PM_{2.5}$ (traffic brake/tire wear, diesel, steel making, and coal) have characteristic chemical patterns, which could be examined in relation to health effects [169-172]. $PM_{2.5}$ toxicity can therefore depend on its source and chemical composition [170]. If a small number of sources contribute significantly to health effects, control strategies could be implemented to focus on those sources [169]. Understanding the sources that contribute to personal exposures is important to interpret health studies [173], and indoor source apportionment is important because individuals spend a large fraction of their life indoors, and indoor concentrations can differ from ambient concentrations [174].

Inductively-coupled plasma mass spectrometry (ICP-MS) analyses were conducted by the Wisconsin State Laboratory of Hygiene following documented protocols (ESS INO Method 400.4; EPA Method 1638) [54]. We performed an updated literature search to find previous source apportionment studies for similar geographic areas in the eastern United States, within the last three decades [50, 111]. Table 19 lists the constituents included in analyses, along with hypothesized sources. For trace metal analyses and indoor combustion sources, common markers for smoking include NO_2, BC, Ca, Cd, Fe, K, and Zn. Common markers for cooking include Al, Ca, Fe, Mn, S, Si, and Zn. Gas stove markers include NO_2 and BC. Tap water can be traced to Ca, K, S, and Si (Table 19).

Table 19. Indoor source apportionment literature review.

Constituents	Indoor Combustion				Indoor Other		
	Smoking	Cooking	Gas Stove	Candles	Soil/ Resuspension	Tap Water	Personal Activities/ Personal Care Products/ Cleaning Products
NO_2	12		12	3			
EC	2, 4, 12		9, 12	8			
Al		32			10, 16		1, 15
As							
Ba							
Ca	2, 8	1, 2, 8			2, 7, 8, 10, 16	14	6
Cd	3, 6, 13						15
Cr							
Cu					2, 5		10, 15
Fe	2, 4	8, 11			2, 7, 16		4
K	1, 2, 4, 7				2, 5, 7, 16	14	6
La	3						
Mg					16		
Mn		11					
Mo							
Ni							15
P					16		10, 15
Pb	2			8	2		15
S	4	2			2	14	15
Sb							
Se					2		
Si	2	1, 6			2, 5, 10	14	6, 15
Sn							
Sr							
V							15
Zn	2, 4	2		8	2		15

Darker shading refers to greater frequency of references: 1 (Zhao, 2007); 2 (Zhao, 2006); 3 (Bohlandt et al., 2012); 4 (Brunekreef, 2005); 5 (Yli-Tuomi, 2008); 6 (Yakoleva, 1999); 7 (Wallace, 1996); 8 (Ozkaynak, 1996); 9 (Lee, 1998); 10 (Koistinen, 2004); 11 (Rizzo and Scheff, 2007); 12 (Lai, 2006); 13 (Kazi, 2010); 14 (Highsmith, 1992); 15 (Hopke, 2003); 16 (Ibanez et al., 2010).

We performed a factor analysis (FA) with varimax rotation (resulting in orthogonal components) using PROC FACTOR in SAS version 9.3 (SAS Institute Inc., Cary, NC). To determine the optimal number of factors, we considered formal criteria including the eigenvalue –one criterion, scree test, and the proportion of variance accounted for, retaining components that account for at least 5% of the total variance. Factor loadings were sensitivity tested using cutoffs of 0.50, 0.60, and 0.70.

Across the 21 monitoring homes, 27 constituents (25 particle constituents from ICP-MS analysis, NO_2 from UV-VIS, and BC from reflectance) were included in factor analysis for each of the two seasons of interest. Concentrations from summer 2011 and winter 2012 are summarized in Tables 20 and 21.

Table 20. Summary of summer 2011 indoor concentrations for the 21 sampled homes, with percent above analytic LOD.

	N (obs)	**Mean**	**Median**	**SD**	**Min**	**Max**	**% > LOD**
$PM_{2.5}$ ($\mu g/m^3$)	21	25.80	20.50	23.22	9.00	121.6	1.00
BC (abs)	21	2.79	2.70	1.17	1.20	5.07	1.00
NO_2 (ppb)	21	13.35	11.80	7.03	3.40	27.90	1.00
Constituents measured by ICP-MS (ng/m^3)							
Al	21	26.02	21.06	14.07	5.67	60.66	1.00
As	21	1.65	1.71	0.87	0.29	4.02	1.00
Ba	21	2.46	2.37	1.28	0.47	5.84	0.67
Ca	21	46.00	37.21	21.82	20.18	103.46	1.00
Cd	21	0.32	0.24	0.36	0.049	1.71	1.00
Ce	21	0.59	0.059	1.39	0.010	5.37	1.00
Cr	21	1.14	1.00	0.87	0.38	4.75	1.00
Cs	21	0.069	0.023	0.083	0.0025	0.29	1.00
Cu	21	3.67	3.37	1.60	0.89	8.49	1.00
Fe	21	104.60	74.15	83.68	16.53	302.50	1.00
K	21	130.41	62.20	245.88	12.32	1136.10	1.00
La	21	0.27	0.036	0.62	0.005	2.49	1.00
Mg	21	11.56	8.53	9.37	3.64	34.75	1.00
Mn	21	5.37	3.58	4.53	0.88	17.08	1.00
Mo	21	1.35	0.96	1.83	0.20	9.09	1.00
Ni	21	0.72	0.60	0.80	0.17	2.45	1.00
P	21	5.96	4.35	7.28	1.49	36.28	1.00
Pb	21	4.75	4.53	2.55	1.51	9.79	1.00
S	21	985.90	866.18	404.13	276.85	1726.05	1.00
Sb	21	0.92	0.86	0.54	0.28	2.33	1.00
Se	21	1.66	1.57	1.27	0.26	6.27	0.90
Sr	21	0.38	0.31	0.20	0.15	0.88	1.00
Tl	21	0.043	0.030	0.038	0.007	0.17	1.00
V	21	0.26	0.23	0.11	0.08	0.53	1.00
Zn	21	34.40	20.61	36.30	5.27	128.14	1.00

Table 21. Summary of winter 2012 indoor concentrations for the 21 sampled homes, with percent above analytic LOD.

	N (obs)	Mean	Median	Std Dev	Min	Max	% > LOD
$PM_{2.5}$ ($\mu g/m^3$)	21	18.93	14.96	13.17	4.75	60.44	1.00
BC (abs)	21	2.29	2.15	1.35	0.094	5.31	1.00
NO_2 (ppb)	21	26.71	18.75	28.77	4.16	138.12	1.00
Constituents measured by ICP-MS (ng/m^3)							
Al	21	24.01	24.49	14.83	0.34	63.89	0.90
As	21	0.57	0.57	0.26	<0.0001	1.01	0.90
Ba	21	1.75	1.12	1.41	<0.0001	5.20	0.71
Ca	21	167.72	54.69	434.48	<0.0001	2034.00	0.90
Cd	21	0.39	0.19	0.52	<0.0001	1.93	0.90
Ce	21	0.96	0.045	2.36	<0.0001	9.44	0.95

Table 21 continued

Cr	21	0.73	0.81	0.46	<0.0001	1.58	0.90
Cs	21	0.036	0.015	0.036	<0.0001	0.11	0.95
Cu	21	2.75	2.20	2.06	<0.0001	8.47	0.90
Fe	21	78.73	54.66	61.75	<0.0001	237.14	0.95
K	21	118.77	54.63	193.42	<0.0001	789.92	0.90
La	21	0.46	0.016	1.15	<0.0001	4.69	1.00
Mg	21	39.63	8.05	134.61	0.15	626.18	0.95
Mn	21	3.97	3.07	3.04	<0.0001	11.78	0.95
Mo	21	0.62	0.57	0.52	<0.0001	1.91	1.00
Ni	21	0.18	0.19	0.24	<0.0001	0.69	0.90
P	21	7.16	3.43	10.84	<0.0001	39.67	0.90
Pb	21	3.70	3.49	2.27	<0.0001	8.99	1.00
S	21	528.46	458.02	503.11	<0.0001	2522.00	0.95
Sb	21	0.59	0.53	0.42	0.0001	1.93	0.90
Se	21	0.42	0.27	0.53	<0.0001	1.51	0.95
Sr	21	0.80	0.31	2.22	<0.0001	10.43	0.90
Tl	21	0.032	0.028	0.028	<0.0001	0.12	0.90
V	21	0.15	0.16	0.074	<0.0001	0.27	0.90
Zn	21	20.72	17.66	15.72	<0.0001	57.25	0.90

For summer 2011, five factors were determined to explain 86% of variability found in trace metals. Factor one was a combination of *smoking* (black carbon, calcium, iron, lead, zinc) and *cooking* (calcium, iron, manganese, zinc) [123, 136, 175-178]. This factor may also include a *steel making* component, since iron, manganese, lead, and zinc were all highly correlated. Factor two includes *smoking*, or *motor vehicle* as cadmium, potassium, and lanthanum were correlated [123, 136, 155, 178-181]. Factor three may be an indicator of *coal*, since arsenic, chromium, nickel, and antimony were correlated [135, 137, 139-141]. Factor four includes *cooking*, as aluminum and calcium were correlated [136, 176, 178]. Factor five indicates *cleaning/personal activities* or *motor vehicle* as sulfur and vanadium were correlated [182]. In all factors except factor three, metals that have been associated with soil/resuspension were detected.

For winter 2012, five factors were also determined to explain 88% of variability found in trace metals. Factor one was a combination of *smoking* (black carbon, cadmium, iron, and lead)

and *cooking* (iron, manganese) [123, 136, 175-177, 179-181]. This factor may also include a *steel making* component, since iron, manganese, and lead were all highly correlated. Factor two includes *smoking*, as nitrogen dioxide, potassium, and lanthanum were correlated [123, 136, 155, 175, 178, 179]. Factor three includes *cooking*, as calcium and sulfur were correlated [136, 176, 178]. Factor four may be an indicator of *coal*, since arsenic, chromium, and nickel were correlated [135, 137, 139-141]. Factor five indicates *cleaning/personal activities* or *motor vehicle* as aluminum, phosphorous, vanadium, and zinc were correlated [182]. In all factors except factor four, metals that have been associated with soil/resuspension were detected.

5.0 SUMMARY/CONCLUSIONS

Pittsburgh's air quality is improving, but intra-urban variability exists. This variability was seen across all methods of sampling, and heightened source contrasts were found during an inversion-focused sampling campaign. Source apportionment methods leveraging the elemental composition of particulate matter helped disentangle urban source contributions, as traffic brake and tire wear, steel making, soil and road dust, and coal factors were determined across various seasons of sampling. Outdoor concentrations and indoor sources contribute to indoor air quality in industrial communities, as outdoor predicted BC from our Pittsburgh LUR models was a significant predictor of indoor air pollution. A combination of these three sampling methodologies can provide a better understanding of public health exposure. Mobile monitoring could be a preliminary first step in any air pollution field study design, since it allows for a quick assessment of pollutant concentrations, and it can provide a better representation of local air pollution. This technique could add a level of stability in location and time specific measures through careful repetition, and it can provide confidence in placement of stationary air samplers. A systematic, repetitive mobile monitoring technique could be employed through community based participatory research, where members of a neighborhood could assess areas, such as high traffic roads and large industrial facilities, where they feel there may be pollution levels exceeding federal EPA standards. Mobile monitoring can determine areas where further

assessment is needed, and this could then be performed via an outdoor saturation campaign, as well as indoor sampling to understand personal exposures.

An outdoor saturation study can cover a large area, where mobile monitoring is not sufficient, and LUR modeling could be used to derive exposure surface maps. Several studies within the Pittsburgh area have determined evidence for PM-dependent health effects, such as cardiovascular disease, asthma, and reproductive outcomes; therefore, exposure surface maps can provide further analyses on health. These maps can provide outdoor-derived pollution estimates that could be tested for indoor sampling. While LUR and multivariate models help explain variability in pollutant concentrations, source apportionment (and an in depth literature review) can provide more specificity into which particular sources are causing the most pollution in any given area. Further LUR and multivariate modeling of the proposed factors can then clarify sources that are not as easily identified. By sampling across an area with these three approaches and developing models and source apportionment, regulations could be enforced on areas that are exceeding federal standards. Since $PM_{2.5}$ is comprised of a combination of acids, trace metals, and dust, studies have been focusing on determining health effects of constituents of $PM_{2.5.}$ Source apportionment allows for characterization of $PM_{2.5}$ across a region, so there could be an emphasis on regulation of trace metals that cause more serious health effects.

Mobile monitors can quickly gauge and measure pollutant levels, such as those for particulate matter, in areas where industrial and/or traffic sources are prevalent. In an effort to characterize PM concentrations in and around Braddock, we identified a seasonal and morning versus afternoon pattern in PM concentrations and observed variability of PM over space and time with a strategically designed mobile sampling protocol. Summertime continuous monitoring led to higher levels compared to the winter, and PM_{10} levels were elevated in the area

near the Edgar Thomson Steel Works. The results point to plant operations related particle emissions as the primary source for PM pollution in and immediately around Braddock.

Because people can spend a significant portion of time indoors, indoor air sampling is an important exposure assessment that cannot be overlooked. Using custom-designed sampling boxes, pollutant concentrations ($PM_{2.5}$, NO_2, BC) were identified throughout a subset of homes in Pittsburgh. These sampling devices could be used in other cities to assess indoor pollution levels, and the questionnaire given to participants could be administered and used for model building purposes. Within the Pittsburgh homes, higher $PM_{2.5}$ concentrations were found during the summer season, whereas higher NO_2 concentrations were found for the winter sampling season. I/O ratios showed that higher $PM_{2.5}$, BC, and NO_2 concentrations were found indoors compared outdoor-predicted LUR estimates from our saturation study. These patterns may differ in other cities, and differences could be attributable to a number of factors, such as smoking, cooking, and outdoor air pollution. The indoor sampling units can provide pollutant information to parents, indicating that daily activities in the home, such as smoking, can lead to higher pollutant concentrations that can harm their children's health. In Braddock and Clairton, indoor activities appear to be stronger sources of pollutant concentrations compared to outdoor-derived LUR estimates, which encompass industrial emissions from the local industries, implying that we should consider establishing health protective indoor air guidelines.

Pollutant concentrations were identified across 37 distributed monitoring locations in Pittsburgh over a period of four seasons and two years. Land use regression models using two sampling methodologies were compared to each other using Pittsburgh as city of interest, and exposure maps were created. Across citywide sampling, mean summer $PM_{2.5}$ and BC concentrations were significantly greater than winter concentrations. For year 1, more inversions

and higher wind speeds occurred in the winter compared to summer. Inversion-sampling produced stronger spatial contrast in source signatures, which can provide clarification of important covariates, and their spatial distribution across a given area. Greater spatial contrasts in $PM_{2.5}$ can better our understanding of source apportionment, in which brake/tire wear, soil and road dust resuspension, steel making, and coal markers were found. For Pittsburgh, land use covariates (commercial and industrial) and industrial emissions were predictors of pollutant variability. Elevation was significant for predicting BC variability during inversion-focused sampling, possibly indicating presence of inversions and trapped local emissions. Exposure surface maps derived from LUR models can now be used in Pittsburgh epidemiological health studies, and the citywide sampling design can be replicated in other cities in a similar manner, with site selections relative to the perspective city's hypothesized source contributions.

Concern about air pollution in the United States was dramatized by extreme pollution episodes, including the 1948 stagnation/smog incident in Donora, Pennsylvania, and the London Smog of 1952. Recently, winter pollutant levels in Beijing, China, are reaching dangerous concentrations; the mobile sampling devices could be used to quickly assess particulate matter in an area of concern such as Beijing. Mobile samplers could provide confidence in where stationary monitors should be deployed. For families worried about the air inside of their home, indoor sampling units could be run to determine a weekly average $PM_{2.5}$ concentration. Quick assessment of an area's pollution can allow for immediate changes, such as smoking and cooking patterns, stove use, ventilation procedures, and distance to industrial/traffic emissions. Other changes could take some time, as land use regression modeling and source apportionment methods can determine the main contributors' of the pollution. A home to community to city hierarchy for analysis can demonstrate pollutant variability and determine significant sources of

pollution. These three methods could be used simultaneously to fully capture an area's pollution. Even though areas in Pittsburgh have concentrations of contaminants that fall below national standards, some fail to do so, and this can therefore affect all who live or travel in the vicinity.

This hierarchy of indoor to citywide sampling can be replicated in other cities of interest, in an attempt to fully understand exposure assessment of multiple pollutants. Though this dissertation focused on $PM_{2.5,}$ BC, and trace metal constituents, other pollutants such as NO_2, O3, SO_2, and organics can be evaluated using similar methodologies. A sampling campaign similar to citywide sampling is currently ongoing in downtown Pittsburgh an attempt to assess $PM_{2.5}$, BC, and trace metal constituents in relation to total traffic, truck traffic, and bus traffic. The air quality in the Pittsburgh region is certainly improving, but areas still remain, which are in federal non-attainment and are at pollution levels affecting public health. Exposure surface maps created from citywide sampling in Pittsburgh can now be used in epidemiological health effect studies, in an effort to understand air pollution and disease. The findings from these exposure assessment studies could be used in policy-making, in an attempt to further clean up Pittsburgh air; this would be followed by targeting the significant sources of pollution and deciding the most beneficial way to handle the issue. Sampling methodologies that were discussed here can be replicated in other cities, as well as repeated in Pittsburgh to gauge improvements in air quality over time. Using these devices in other cities, factors such as distance to industrial sources or high traffic density, elevation grade, season, time of day, and presence of atmospheric inversions can be considered. By fully understanding pollution sources, we can make Pittsburgh an even healthier, more environmental friendly city. This dissertation focused on a public health approach geared toward protecting communities using the results from exposure assessment and subsequent development of models, exposure surface maps, and source apportionment.

Conclusions from this dissertation:

- Pittsburgh air quality has improved over time, but certain industrial and high traffic areas, along with the combination of unique terrain and meteorological events result in intra-urban variability.
- Source apportionment methods leveraging the elemental composition of particulate matter helped disentangle urban source contributions, as traffic brake/wear, soil/road dust, steel making, and coal factors were determined.
- Outdoor concentrations and indoor sources contribute to indoor air quality in industrial communities, and smoking is the most important predictor for fine particulate matter and black carbon concentrations.
- Exposure pollutant surface maps from citywide sampling in Pittsburgh can now be used in epidemiological health effects studies.
- Sampling methodologies could be replicated in other cities, with an emphasis on observing more pollutant spatial variability during peak hours, which may be more predictive of health outcomes.
- Exposure patterns differ by constituents, signaling different sources of pollution, so it may be important to consider a variety of regulatory approaches.

APPENDIX A

INDOOR AIR QUESTIONNAIRE

The following questionnaire was administered to participants for indoor air sampling and answers were used for multivariate modeling purposes.

Indoor Air Pollution Questionnaire

Multi-Level Analysis of Urban Childhood Asthma Risk
FOR AIR POLLUTION SAMPLING

INTERVIEWER ID: 10-Brett, 11-Leah [ ][ ]

DATE OF INTERVIEW: [ ][ ] / [ ][ ] / [ ][ ]
Month Day Year

BEGIN TIME: [ ][ ]: [ ][ ] AM/PM

LANGUAGE OF INTERVIEW
1 - English
2 – Other (describe) [ ]

(CODE FOR ALL QUESTIONS)
Instructions to interviewers: If the answer to any of the questions is "I don't know," then please fill the box with the number 9. If the respondent chooses not to answer a question or if the question does not relate to the respondent, then please leave the box blank.

DON'T KNOW [9][9] or [9]

I would like to begin by asking you some questions about the activities in your home in the last week. This information will help us figure out what might be affecting air pollution inside your home. All of the information you give me will be kept confidential and used for research purposes only. If you do not know the answer to any of the questions, please answer "Don't Know."

FOR OFFICE USE ONLY

Data Entry Date: ____/____/____ Data Entry Initials: _____

ES1. In the last week, counting yourself, how many people spent more than 4 hours per day, on average, in your home?

___ ___ people

a) How many of these people are adults (age 18 and older)?

___ ___ adults

b) How many of these people are children (age 17 or under)?

___ ___ children

ES2. On a typical day in the last week, about how many hours did <<CHILD>> spend:

at home? ___ ___ hours

at someone else's home? ___ ___ hours

If more than four hours

Where is this home located (street and city)?

_____

at day care? ___ ___ hours

If more than four hours:

Where is the day care facility located (street and city)?

_____

in transportation (like a car, bus, or train)? ___ ___ hours

outdoors? ___ ___ hours

ES3. In the last week, approximately how many cigarettes per day were smoked, in total, by all smokers inside your home?

1 - Less than 1 cigarette per day
2 - 1 to 4 cigarettes per day
3 - 5 to 14 cigarettes per day
4 - 15 to 24 cigarettes per day
5 - 25 cigarettes or more per day
9 – Don't know

☐

ES4. In the last week, how many days did you use your stove or oven for cooking?

___ ___ days

ES5. In the last week, how many days did you use your stove or oven for frying, grilling, sautéing, or broiling?

___ ___ days

ES6. In the last week, what was the average length of time that you used your stove or oven for cooking each day?

___ ___ hours
___ ___ minutes

ES7. In the last week, did you ever use a charcoal grill inside your home?

0 – No
1 – Yes
9 – Don't Know

☐

ES8. In the last week, did you ever cook meat?

0 – No
1 – Yes
9 – Don't Know

☐

ES9. In the last week, did you use the exhaust fan when cooking?

0 – No
1 – Yes
9 – Don't Know

☐

ES10. In the last week, did you burn any food (like toast)?

0 – No
1 – Yes
9 – Don't Know

☐

ES11. In the last week, how drafty would you consider your home?

1 – Very drafty
2 – About average
3 – Not drafty at all
9 – Don't know

☐

ES12. In the last week, did you ever need to supplement your primary heating system?

0 – No
1 – Yes
9 – Don't Know

☐

a) What type of system did you use to supplement your primary heating system?

1 – Electric space heater

2 – Kerosene space heater

3 - Solar

4 – Wood burning stove

5 – Gas/electric stove

6 - Fireplace ☐

7 – Other, please specify _____

ES13. Does your home have air conditioning?

0 – No
1 – Yes
9 – Don't Know

☐

a) In the last week, how often did you use air conditioning? ☐

1 - Never

2 – Less than once a week

2 – 1-2 times a week

ES14. In the last week, on average, about how many hours were the windows open?

1 - Less than 1 hour
2 – 1-4 hours
3 – 5-12 hours ☐

4 – More than 12 hours
9 – Don't know

ES15. In the last week, did you use an ultrasonic or "cool mist" humidifier in your home?

0 – No
1 – Yes
9 – Don't Know

☐

a) What type of water did you use in the humidifier?

1 – Tap water ☐

2 – Other (bottled, distilled, etc.)

ES16. In the last week, did you use a "warm mist" humidifier in your home?

0 – No
1 – Yes
9 – Don't Know

☐

a) What type of water did you use in the humidifier?

1 – Tap water ☐

2 – Other (bottled, distilled, etc.)

ES17. In the last week, did you use an air cleaner/ purifier in your home?

0 – No
1 – Yes
9 – Don't Know

☐

a) What brand is it?

ES18. In the last week, about how often did you burn candles or incense?

1 - Never
2 – Less than once a week
3 – 1-2 times a week
4 – 3-5 times a week
5 – Every day
9 – Don't know

☐

ES19. In the last week, did members of your family regularly wear shoes inside the house?

0 – No
1 – Yes
9 – Don't Know

☐

ES20. In the last week, did members of your family engage in any of the following cleaning activities:

Circle the appropriate answer in the boxes below.

a) Swept floors in your home?	0 – No	1 – Yes	9 – Don't Know
b) Washed floors in your home?	0 – No	1 – Yes	9 – Don't Know
c) Dusted surfaces?	0 – No	1 – Yes	9 – Don't Know
d) Vacuumed?	0 – No	1 – Yes	9 – Don't Know
e) Washed or cleaned upholsteries (like furniture or drapes)?	0 – No	1 – Yes	9 – Don't Know

ES21. Do you use a doormat at your front door?

0 No
1 Yes, an outdoor doormat
2 Yes , an indoor doormat
3 Yes, a doormat indoor and outdoor

☐

E22. In a typical week, how often do you clean the kitchen?

1 – Never (skip to E23)
2 – Less than once a week
3 – 1-2 times a week
4 – 3-5 times a week
5 – Every day
9 – Don't know

E22a. What products do you use?

1 _____
2_____
3_____

E23. How frequently do you clean the oven?

1 – Never
2 – Daily
3 – Weekly
4 – Monthly
5 – Every few months
9 – Don't know

E24. How frequently do you clean the bathroom?

1 – Never (skip to E25)
2 – Daily
3 – Weekly
4 – Monthly
5 – Every few months
9 – Don't know

E24a. What products do you use?

1 _____
2_____
3_____

E25. How frequently do you polish the furniture?

1 – Never
2 – Daily
3 – Weekly
4 – Monthly
5 – Every few months
9 – Don't know

E26. How often do you use solvents – things like products to remove oil and grease, rubbing alcohol or nail polish remover – in your home?

1 – Never
2 – Daily
3 – Weekly
4 – Monthly
5 – Every few months
9 – Don't know

E27. Do you ever mix cleaning products?

0 - No
1 – Yes
2 – Don't know

E28. Do you typically use scented products (e.g. lemon, pine or other scent)?

0 - No
1 – Yes
2 – Don't know

E29. Are any of your cleaning products in spray form?

0 – No (skip to E30)
1 – Yes
2 – Don't know

E29a. If yes, what spray products do you use?

1 _____
2_____
3_____

E29b. How frequently do you use these products?

1 – Daily
2 – Weekly
3 – Monthly
4 – Every few months
9 – Don't know

E30. How frequently do you use any type of air fresheners (e.g. plug in air fresheners or bathroom sprays)?

1 – Never
2 – Daily
3 – Weekly
4 – Monthly
5 – Every few months
9 – Don't know

Have you ever had a pet?

0 - No
1 – Yes

Do you have a pet or does any animal frequently spent time in your home?

0 - No
1 – Yes (go to next question)

If yes, what kind of pet(s)?

1 – Cat (if multiple animals, note number___)
2 – Dog (if multiple animals, note number___)
3 – Bird (if multiple animals, note number___)
4 – Other_____ (if multiple animals, note number___)

Which, if any, rooms in your home are carpeted?

1 – Living/Family room
2 – Adult bedroom
3 – Child bedroom
4 – Dining room
5 – Other

Have you ever seen evidence of pests in your home such as:

Mice	0 – No	1 – Yes	9 – Don't Know
Cockroaches	0 – No	1 – Yes	9 – Don't Know
Other insects	0 – No	1 – Yes	9 – Don't Know

Have you ever used any pesticides in your home?

0 - No
1 – Yes
2 – Don't know

If yes, what pesticides do you use?

1 _____
2_____
3_____

ES24. (observe) Is there any visible mold present in the house?

0 No
1 Yes

APPENDIX B

CITYWIDE SITE SURVEY

SITE SURVEY FORM: CITYWIDE CAMPAIGN

Date: **Time:** **Surveyor(s):**

LOCATION OF STARTING POINT

Lattice Cell ID#:
Latitude:
Longitude:
Elevation:

Street Segment (Nearest Address):
Cross Street A (Name and direction from post):
Cross Street B (Name and direction from post):
Borough:

SECTION 1- ACCEPTABILITY CRITERIA

A. INITIAL CRITERIA

Unit cells of interest will be printed out, and the nearest address will be used to travel to a particular cell. The first considered post in the cell will be assessed as site 1, and recorded in the first column of this form. If this pole is rejected, continue using a new column for each new post, until an acceptable post is identified.

B. EXCLUSION CRITERIA

Lamp/Signal Post Criteria I	1		2		3		4		5		6		7		8	
	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N
1. 9 or more feet away from building or scaffolding?																
2. At least 3 feet away from tree branches?																
3. Not exposed to air flow from exhaust vents?																
4. At least 25 feet away from mobile food carts with cooking/grilling?																
5. At least 25 feet away from a ventilation grate?																

C. SECONDARY CONSIDERATIONS

Lamp/Signal Post Criteria II	1		2		3		4		5		6		7		8	
	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N
6. Free from street resurfacing activities?																
7. At least 50 feet away from mobile food cart with cooking or grilling?																
8. At least 50 feet from ventilation grates?																
9. Free of any other mountings above 12 ft?																
10. At least 25 feet away from areas where smokers congregate?																
STATUS (Circle one)	A AR R		A AR R		A AR R		A AR R		A AR R		A AR R		A AR R		A AR R	

SECTION 2- LAMP POST INFORMATION

Lattice Cell ID#:

Survey Post Number (from page 1):

Pole ID#:

Latitude (GPS reading):

Longitude (GPS reading):

Street Segment (Nearest Address):

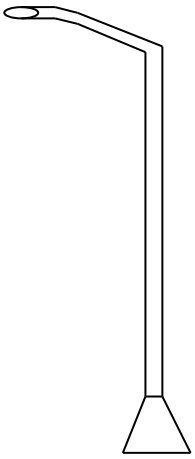
Cross Street A (Name and direction from Street Segment):

Cross Street B (Name and direction from Street Segment):

1. **Is post located at signaled intersection?**

2. **Tree cover above post (0-3)?**

3. **What objects are currently mounted on the post and their heights (sketch on diagram)?**



4. **Street cleaning schedule and site access information?**

5. **Digital photo numbers**

SECTION 3- STREET SEGMENT INFORMATION

Lattice Cell ID#:

Survey Post Number (from page 1):

Street Segment (Nearest Address):

Cross Street A (Name and direction):

Cross Street B (Name and direction):

1. Road and Traffic Types (insert number from key) TIME:

Category	Segment	Cross Street A	Cross Street B
Road Type			
Car Traffic			
Truck Traffic			

2. Land Use Characteristics (Check all that apply):

Land Use Type	Segment	Cross Street A	Cross Street B
Residential			
Commercial			
Industrial			
Government			
Open Area			

3. Tree cover above sidewalk (0-3)?

4. Street Characteristics (Circle any that apply and write letter at location on map)

A) Auto Body/Repair Shops **B) Parking Garage**

C) Street Resurfacing Operations (describe) **D) Construction Sites (describe)**

E) Other Activities (describe):

5. Bus Stops?

6. Comments

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